SOLUTION OF THE PHASE PROBLEM IN SURFACE X-RAY DIFFRACTION: THEORY AND APPLICATIONS TO EXPERIMENTAL DATA

by

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ABSTRACT

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Under the supervision of Prof. Dilano K. Saldin

Lack of phase information in typical x-ray diffraction measurements makes it very difficult to recover the atomic-scale structure of a crystal by direct inversion of the measured amplitudes. We have developed a direct method for surface x-ray diffraction (SXRD) to recover the part of the surface structure that is different from the truncated bulk. The iterative algorithm we have developed employs prior knowledge of the bulk structure and alternately satisfies constraints in real and reciprocal space.

Our method has recently been applied on experimental SXRD data of the known clean Au (110) (1×2) reconstruction as well as the unknown Sb/ Au (110) c(2×2) and Sb/ Au (110) \((\sqrt{3} \times \sqrt{3}) R54.7^\circ\) reconstructions.

We were able to recover all the features of the clean Au (110) (1×2) reconstruction previously established by researchers using different experimental techniques, including missing row, first-layer contraction, second-layer expansion, third-layer buckling and second- and fourth-layer pairing. None of the previous studies was able to show
all these features.

Our results for Sb/ Au (110) \( c(2 \times 2) \) reconstruction suggested a model in which Sb adatoms occupied every other surface substitutinal site, the rest occupied by Au adatoms, forming a checkerboard pattern.

For the Sb/ Au (110) \( (\sqrt{3} \times \sqrt{3}) \ R54.7^\circ \) system, our direct-method algorithm was adapted to deal with the presence of four symmetry-related domains. Our results suggested a model in which two Sb adatom diagonal rows alternated with a row of Au adatoms, all adatoms in surface substitutional sites.

In both of these unknown structures, quantitative conventional refinement of these suggested starting models yielded good agreement with the scattering data, supporting the veracity of the starting models.
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Chapter 1

Introduction

1.1 Surface X-Ray Diffraction (SXRD), Phase Problem and Conventional Method for Structure Determination

Amplitudes \( \{F(\vec{q})\} \) of x-rays scattered off a system of interest can be expressed as the discrete Fourier transform of its electron distribution \( \{u(\vec{r})\} \).\(^1\) In particular,

\[
F_{\vec{q}} = |F_{\vec{q}}| \exp(i\phi_{\vec{q}}) = \sum_j u(\vec{r}_j) \exp(2\pi i \vec{q} \cdot \vec{r}_j),
\]

(1.1)

where the sum is over a set of grid points in a real space unit cell. In Eq. (1.1), \( \vec{r} \) is a real space coordinate triplet and \( \vec{q} \) is a momentum transfer vector.\(^2\) The components of \( \vec{r} \) are usually expressed as fractions \( (x, y, z) \) of the basis of a real space unit cell:

\[
\vec{r} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3,
\]

(1.2)

while the vector \( \vec{q} \) is usually expressed in terms of multiples \( (hkl) \) of the basis vectors of a unit cell of the reciprocal lattice:

\[
\vec{q} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3.
\]

(1.3)

The basis vectors for real lattice \( \{\vec{a}\} \) and reciprocal lattice \( \{\vec{b}\} \) are related through \( \vec{a}_i \cdot \vec{b}_j = \delta_{ij} \), and \( (hkl) \) are referred to as Laue indices.

\(^1\)The Fourier transform relation between scattering amplitudes \( \{F(\vec{q})\} \) and electron densities \( \{u(\vec{r})\} \) is derived in Appendix A.

\(^2\)\( \vec{q} = \vec{k} - \vec{k}_0 \), where \( \vec{k}_0 \) and \( \vec{k} \) are respectively wavevectors of the incident and scattered x-rays.
In principle, if both the magnitudes \( \{|F(\vec{q})|\} \) and phases \( \{\phi(\vec{q})\} \) of these scattering amplitudes are measured, the electron densities over a set of grid points, and consequently the atomic distribution, of our system of interest can be recovered via a simple inverse Fourier transform:

\[
u(\vec{r}) = \frac{1}{N} \sum_{\vec{q}} |F_{\vec{q}}| \exp(i\phi_{\vec{q}}) \exp(-2\pi i \vec{q} \cdot \vec{r}),
\]

(1.4)

where \( N \) is the number of terms (or Fourier components) in the sum.\(^3\)

In Surface X-Ray Diffraction (SXRD), scattering amplitude (or structure factor) \( F_{\vec{q}} \) can be considered to consist of two components \( B_{\vec{q}} \) and \( S_{\vec{q}} \), representing respectively the contribution of the known bulk and the unknown surface layer, such that

\[
F_{\vec{q}} = B_{\vec{q}} + S_{\vec{q}}.
\]

(1.5)

Again, if both the magnitudes and phases of scattering amplitudes \( \{F(\vec{q})\} \) are measured, then in principle, contribution from the known bulk \( \{B(\vec{q})\} \) can be calculated and subtracted out to give the surface contribution \( \{S(\vec{q})\} \), from which the electron densities \( \{u_S(\vec{r})\} \) of the unknown surface layer over a set of grid points, and consequently the atomic distribution in the unknown surface layer of our system, can be recovered via a simple inverse Fourier transform:

\[
u_S(\vec{r}) = \frac{1}{N} \sum_{\vec{q}} S_{\vec{q}} \exp(-2\pi i \vec{q} \cdot \vec{r}) = \frac{1}{N} \sum_{\vec{q}} |S_{\vec{q}}| \exp(i\theta_{\vec{q}}) \exp(-2\pi i \vec{q} \cdot \vec{r}).
\]

(1.6)

In an x-ray diffraction experiment, intensities (not amplitudes) of x-rays reflected.

\(^3\) Fourier transforms are usually performed on a computer using Fast Fourier Transform (FFT) subroutines, for which the number of grid points in a real space unit cell is taken to be the same as the number of Fourier components, which, for experimental data, is the same as the number of inequivalent scattering amplitudes measured.
off a sample of interest are collected as a function of incident and reflected angles (corresponding to different momentum transfer vectors.) These intensities are proportional to the squares of the scattering amplitudes, the magnitudes of which can therefore be recovered by taking square roots of the measured intensities. However, the corresponding phases are not generally measured. This is the famous phase problem.

Despite the lack of phase information, atomic structures are routinely solved using x-ray diffraction data. The in-plane \((l \approx 0)\) diffraction pattern can be analyzed to yield the shape and dimensions of a surface unit cell, and, for multi-domain systems, the number of surface domains and the symmetry relations between them.

If the structure of the bulk is assumed to be known, then given any atomic model of the surface structure, the expected distribution of scattered x-rays can be calculated (Vlieg et al. 1989):

\[
B_{\bar{q}} = \sum_j f_j(\bar{q}) \exp \left(-\frac{B_j q^2}{4}\right) \frac{\exp(2\pi i \bar{q} \cdot \vec{r}_j)}{1 - \exp(-2\pi il) \exp(-\alpha)}
\]

\[
S_{\bar{q}} = \sum_j f_j(\bar{q}) \exp \left(-\frac{B_j q^2}{4}\right) \exp(2\pi i \bar{q} \cdot \vec{r}_j).
\]

The sums here are over all atoms \(j\), at positions \(\vec{r}_j\), with form factors \(f_j(\bar{q})\) and Debye-Waller factors \(B_j\), in a bulk (for \(B_{\bar{q}}\)) or surface (for \(S_{\bar{q}}\)) unit cell. \(\alpha\) is the attenuation coefficient for x-ray in the crystal bulk and the factor \(1/[1 - \exp(-2\pi il) \exp(-\alpha)]\) is the result of summing up the contributions of all the bulk layers.

Simulated structure factors can be compared with experimentally obtained ones, and a measure of discrepancy, e.g. a measure \(\chi^2\) of least-squares fit, can be calculated
for this model structure:

$$\chi^2 = \frac{1}{N} \sum_{\vec{q}} \left[ \frac{|F_{\vec{q}}^{\text{obs}}| - c|F_{\vec{q}}^{\text{calc}}|}{\sigma_{\vec{q}}} \right]^2. \quad (1.9)$$

Here $|F_{\vec{q}}^{\text{obs}}|$ and $|F_{\vec{q}}^{\text{calc}}|$ are respectively the magnitudes of measured and calculated total structure factors for momentum transfer vector $\vec{q}$. $\sigma_{\vec{q}}$ is the uncertainty in the determination of $|F_{\vec{q}}^{\text{obs}}|$. The sum is over all the inequivalent momentum transfer vectors for which measurements have been made. Since x-ray intensities are not usually measured on an absolute scale, scaling factor $c$ is chosen so that $\chi^2$ is minimized:

$$c = \frac{\sum_{\vec{q}} \left( \frac{|F_{\vec{q}}^{\text{obs}}|}{|F_{\vec{q}}^{\text{calc}}|} \right)^2}{\sum_{\vec{q}} \left( \frac{|F_{\vec{q}}^{\text{calc}}|}{\sigma_{\vec{q}}} \right)^2}. \quad (1.10)$$

A $\chi^2$ value of about 2 or smaller indicates a good agreement between the trial structure and the correct one. If necessary, a process of refinement can be performed, in which position, vibrational amplitude$^4$ and occupancy of each of the surface atoms in the trial model, abundance of each of the symmetry-related domains and roughness$^5$ of the surface are treated as fitting parameters.$^6$ In this conventional, trial-and-error method the correct structure is taken as the one that minimizes the measure of discrepancy.

Conventional analysis, as the above method of structure determination has come to be known, is essentially a process of refinement of an initial trial model. Trial models can be obtained using chemical intuition, symmetry consideration, knowledge of related systems or a map of the autocorrelation function (discussed in Sec. 1.3.) Due to an

---

$^4$Debye-Waller factor $B$ and mean-square vibrational amplitude $<(\Delta r)^2>$ of an atom are related by $B = 8\pi^2 <(\Delta r)^2>$. This is derived in Sec. A.2.

$^5$See Robinson (1991) for a discussion on surface roughness.

$^6$Vlieg’s ROD is a software package widely used by researchers for this model-refinement process.
almost unlimited number of possible starting models, there is no guarantee that an appropriate one may be guessed that will refine to the correct structure.

1.2 Choice of Basis Vectors, Diffraction Rods and Surface Reconstruction

In SXRD, real space basis vectors \( \{ \vec{a} \} \) are customarily chosen so that \( \vec{a}_1 \) and \( \vec{a}_2 \) are parallel to the surface of a sample, and \( \vec{a}_3 \) is normal to the surface. If basis vectors are chosen to be those of a bulk unit cell, then scattering amplitudes with integer Laue indices arise from real space features having the same periodicity as the bulk.

The presence of a surface breaks the 3D periodicity of a bulk crystal in the direction normal to the surface. Bragg spots broaden into streaks in this direction and the resultant continuous distribution of scattering intensities is referred to as diffraction rods (Andrews and Cowley (1985), Robinson (1986)).

If a surface reconstructs so that the dimensions of its 2D unit cell (parallel to the surface) are larger than those of the bulk, nonzero diffraction intensities can be measured for certain momentum transfer vectors with noninteger values of either or both of the in-plane Laue indices \( h \) and \( k \) (Eq. (1.3)). In the simplest case in which the 2D lattice vectors for the surface are \( \alpha \vec{a}_1 \) and \( \beta \vec{a}_2 \) where \( \alpha \) and \( \beta \) are positive integers, and \( \vec{a}_1 \) and \( \vec{a}_2 \) are the 2D lattice vectors for the bulk, nonzero diffraction intensities can be measured at \( (h, k) = \left( \frac{m}{\alpha}, \frac{n}{\beta} \right) \), where \( m \) and \( n \) are integers. Due to the finite vertical extent of the surface layer, these diffraction intensities are also continuous.
along the direction normal to the surface. Diffraction rods with integer in-plane Laue
indices are called *Crystal Truncation Rods* (CTRs) and those with noninteger values
of either or both of the in-plane Laue indices are called *Superstructure Rods* (SRs).
CTR reflections have contributions from both the crystal bulk and the surface layer:

\[ F_{\mathbf{q} \in \{ \mathbf{q}_{\text{CTR}} \}} = B_{\mathbf{q}} + S_{\mathbf{q}}, \]

(1.11)

whereas SR reflections only have contribution from the surface layer:

\[ F_{\mathbf{q} \in \{ \mathbf{q}_{\text{SR}} \}} = S_{\mathbf{q}}. \]

(1.12)

### 1.3 Patterson Function

A Patterson function is the autocorrelation function of the electron density distri-
bution, and as such, its peaks correspond to the peak-to-peak vectors of the electron
density distribution. In other words, a Patterson function is a map of interatomic
vectors.

Since we are mostly interested in the electron density distribution in the surface
layer of a system, we will define Patterson function as the autocorrelation function of
the electron density distribution of just the surface region \( \{ u_S(\mathbf{r}_j) \} \):

\[ P(\mathbf{r}) = \sum_j u_S(\mathbf{r}_j) u_S(\mathbf{r}_j + \mathbf{r}), \]

(1.13)

where the sum is over the set of grid points on which \( \{ u_S(\mathbf{r}) \} \) is defined. With this
definition, a Patterson function is a map of interatomic vectors of the surface region.

Substituting Eq. (1.6) into Eq. (1.13):

\[
P(\vec{r}) = \frac{1}{N^2} \sum_{\vec{q}\vec{q}'} |S_{\vec{q}}||S_{\vec{q}'}| \exp(i(\theta_{\vec{q}} + \theta_{\vec{q}'}) \exp(-2\pi i(\vec{q} + \vec{q}') \cdot \vec{r}_j) \exp(-2\pi i\vec{q}' \cdot \vec{r}),
\]

\[
= \frac{1}{N} \sum_{\vec{q}} |S_{\vec{q}}||S_{-\vec{q}}| \exp(i(\theta_{\vec{q}} + \theta_{-\vec{q}})) \exp(2\pi i\vec{q} \cdot \vec{r}),
\]

\[
= \frac{1}{N} \sum_{\vec{q}} |S_{\vec{q}}|^2 \exp(2\pi i\vec{q} \cdot \vec{r}),
\]

(1.14)

where we have used the normalization:

\[
\sum_j \exp(-2\pi i(\vec{q} + \vec{q}') \cdot \vec{r}_j) = N\delta_{\vec{q},-\vec{q}},
\]

(1.15)

and Friedel’s Law:

\[
S_{-\vec{q}} = S_{\vec{q}}^*, \quad |S_{-\vec{q}}| = |S_{\vec{q}}|, \quad \theta_{\vec{q}} + \theta_{-\vec{q}} = 0,
\]

(1.16)

to simplify the result.

Since electron density is a real function, the Patterson function (Eq. (1.13)) is real. Eq. (1.14) can therefore be written as

\[
P(\vec{r}) = \frac{1}{N} \sum_{\vec{q}} |S_{\vec{q}}|^2 \exp(-2\pi i\vec{q} \cdot \vec{r}),
\]

(1.17)

or

\[
P(\vec{r}) = \frac{1}{N} \sum_{\vec{q}} |S_{\vec{q}}|^2 \cos(2\pi \vec{q} \cdot \vec{r}).
\]

(1.18)

Eq. (1.17) states that Patterson function is the inverse Fourier transform of the surface scattering intensities. Calculating this function would allow one to identify all the interatomic vectors present in the surface layer of the sample of interest and thus
put constraints on and reduce the number of possible starting models for conventional analysis.

However, short of recovering the phases of the measured scattering amplitudes and thus solving the structure, there is no easy way to separate out the surface contribution \( \{ S_{\vec{q}} \} \) to CTR reflections (Eq. (1.11)). The Patterson function for SXRD data is, therefore, calculated using only experimentally measured SR reflections \( \{ \vec{q}_{SR} \} \), hence the name \textit{fractional} Patterson function.

Traditionally, only in-plane data are used in calculating the fractional Patterson function:

\[
P(\vec{r}) = \frac{1}{N} \sum_{\vec{q} \in \{ \vec{q}_{SR}, l=0 \}} |S_{\vec{q}}|^2 \cos(2\pi \vec{q} \cdot \vec{r}),
\]  

(1.19)

which is the 2D projection of the surface-layer interatomic vectors onto a plane parallel to the surface of the system.

Since the fractional Patterson function is calculated using only SR reflections, it should not come as a surprise that sometimes certain interatomic vectors that appear in a surface structure do not show up in its fractional Patterson map.

Bohr et al. pointed out in 1986 that while the fractional Patterson function of a surface structure might not contain all the interatomic vectors that appear in the surface structure, it also cannot have false positive peaks, i.e. all positive peaks in the fractional Patterson map must correspond to interatomic vectors in the surface structure.

We have found that for systems with certain symmetries, regardless of the actual surface structure, a Patterson map calculated using only SR reflections will have a
negative peak at any interatomic vector that corresponds to a 2D bulk lattice vector unless that vector also corresponds to a 2D surface lattice vector. We will show in Chapters 6 and 7 that this is the case for the Sb/ Au(110) \( c(2 \times 2) \) and Sb/ Au(110) \( (\sqrt{3} \times \sqrt{3}) \) \( R54.7^\circ \) systems.

Even in the absence of this pathological problem, a Patterson map gets more and more complicated as the number of atoms in a surface unit cell increases, and can become too complex to analyze easily.

### 1.4 Direct Methods

Direct methods for SXRD aim to produce an image of the electron densities in the surface region directly from experimental x-ray diffraction data, independent of models. The image is interpreted to give an atomic model which can then be refined by conventional means. The main purpose of a direct method is not to replace conventional analysis, but to arrive at a good trial model for subsequent refinement. In particular, direct methods try to recover the phase information that is missing from the experimental data, and then directly invert the surface structure factors to obtain the electron densities in the unknown surface layer (Eq. (1.6)).
1.5 Structure of the dissertation

This dissertation is on the theory and applications of a direct method developed to solve the phase problem in surface x-ray diffraction (SXRD). Chapter 2 gives the theoretical background as well as discusses the various ingredients that go into our direct-method algorithm. Chapter 3 introduces our experimental test system: Au(110). Reduction of experimental data is the focus of Chapter 4, although detailed experimental setups and conditions will not be discussed. Applications of our direct-method algorithm to experimental SXRD data to solve the surface structures of the well-known clean Au(110) (1×2) system, and the unknown Sb/ Au(110) c(2×2) and Sb/ Au(110) \((\sqrt{3} \times \sqrt{3})\ R54.7^\circ\) systems are the subjects of Chapters 5, 6 and 7 respectively. Some conclusions will be given in Chapter 8.
2.1 Introduction

Direct methods in x-ray diffraction aim to remove the need for an initial inspired guess for a trial model, but instead obtain rapidly from the measured data an approximate model of the structure that can be refined by conventional methods. Although direct methods have a long history in the field of bulk x-ray diffraction, their application to surface x-ray diffraction is still in its infancy.

Our direct-method algorithm has its origin in the work of Gerchberg and Saxton (1972), Fienup (1978, 1982) and Miao et al. (1999). These are to be described in Sec. 2.2, followed by details of our direct-method algorithm in Sec. 2.3.
2.2 Ingredients of a Direct Method

2.2.1 Gerchberg-Saxton loop

Gerchberg and Saxton presented in 1972 an algorithm to solve for the phases of a complex wave function whose intensities in both Fourier space \( I(\vec{q}) = |F(\vec{q})|^2 \) and object space \( i(\vec{r}) = |f(\vec{r})|^2 \) are known and where the complex amplitudes \( \{F(\vec{q})\} \) and \( \{f(\vec{r})\} \) are related by Fourier transforms:

\[
\{F(\vec{q})\} = FT(\{f(\vec{r})\}), \quad (2.1)
\]
\[
\{f(\vec{r})\} = FT^{-1}(\{F(\vec{q})\}). \quad (2.2)
\]

The most important feature of this algorithm is an iteration scheme (Fig. 2.1) in which constraints are alternately imposed in diffraction and object planes. The goal is to obtain phase estimates that improve as more iterations are performed. While inside the loop, (a) a complex wave function \( \{G(\vec{q})\} \) that satisfies the diffraction-domain constraints is inverse Fourier transformed to give \( \{g(\vec{r})\} \) in object plane. \( \{g(\vec{r})\} \) would not, in general, satisfy the object-domain constraints. (b) \( \{\Delta g(\vec{r})\} \) is added to \( \{g(\vec{r})\} \) so that the sum \( \{g(\vec{r})\} = \{g(\vec{r})\} + \{\Delta g(\vec{r})\} \) conforms to the object-domain constraints. (c) \( \{g(\vec{r})\} \) is then Fourier transformed to give \( \{G(\vec{q})\} \) in Fourier plane. Again, \( \{G(\vec{q})\} \) would not, in general, satisfy the diffraction-domain constraints. (d)

---

1Fourier space is sometimes referred to as “diffraction space”, “reciprocal space”, “Fourier plane”, “diffraction plane”, “Fourier domain” or “diffraction domain”. These terms can be used interchangeably in discussions of surface x-ray diffraction. Similarly the terms “object space”, “object plane”, “image space”, “image plane”, “real space” and “object domain” all have the same meaning in surface x-ray diffraction.
\{\Delta G(q)\} is added to \{G(q)\} so that the sum \{G'(q)\} = \{G(q)\} + \{\Delta G(q)\} conforms to the diffraction-domain constraints, and the cycle repeats.

Gerchberg and Saxton suggested starting the iteration by assigning random phases \{\phi_0(q)\} to the experimentally obtained diffraction magnitudes \{|F(q)|\} and enter the loop at step (a) with \{G_1(q) = |F(q)| \exp(i\phi_0(q))\}. It is also possible to begin at step (c) with \{g_1(r) = |f(r)| \exp(i\theta_1(r))\} after assigning random phases \{\theta_1(r)\} to the experimentally obtained object magnitudes \{|f(r)|\}.

The phase problem is solved when functions \{\tilde{G}(q)\} and \{\tilde{g}(r)\} = FT^{-1}(\{\tilde{G}(q)\}) are found that respectively satisfies constraints in diffraction and object domains.

![Figure 2.1 Schematic flowchart of the Gerchberg-Saxton loop.](image)

When experimental data are available in either or both diffraction and object planes, the most obvious and sensible diffraction-/object-domain constraint to apply is conformity to experimental data. For instance, if diffraction intensities \{I(q) =
\(|F(\vec{q})|^2\) are available, then in step (d) of the Gerchberg-Saxton loop, magnitude of each member of \(\{G(\vec{q})\}\) can be adjusted to match that of the corresponding member in \(\{|F(\vec{q})|\}\), while keeping its phase angle unchanged. This is illustrated in Fig. 2.2. A similar procedure can be performed in step (b) of the Gerchberg-Saxton loop if object intensities \(\{i(\vec{r}) = |f(\vec{r})|^2\}\) are available (Fig. 2.3).

![Figure 2.2](image-url)

**Figure 2.2** Schematics showing how diffraction-domain constraints are enforced by magnitude adjustment in the Gerchberg-Saxton loop. \(G_{\vec{q},n}\) is (a) shortened, (b) lengthened, (c) kept unchanged, while its phase angle remains unchanged, to give \(G'_{\vec{q},n+1}\) whose magnitude equals \(|F_{\vec{q}}|\).

In the original Gerchberg-Saxton algorithm, devised for use in electron microscopy, intensities in both diffraction and object planes are assumed to be available, therefore, diffraction- and object-domain constraints are enforced using the *magnitude-adjustment* operation described above and illustrated in Figs. 2.2 and 2.3. Phases \(\{\theta(\vec{r})\}\) and \(\{\phi(\vec{q})\}\) of the Fourier tranforms \(\{g(\vec{r})\}\) and \(\{G(\vec{q})\}\) are taken as estimates, for the current iteration, of the correct phases in object plane and diffraction plane respectively. These phase estimates are combined with the experimentally obtained magnitudes \(\{|f(\vec{r})|\}\) and \(\{|F(\vec{q})|\}\) to give estimates, for the current iteration,
Figure 2.3 Schematics showing how object-domain constraints are enforced by magnitude adjustment in the original Gerchberg-Saxton algorithm where object-plane intensities are assumed to be available. $g_n(\vec{r}_j)$ is (a) shortened, (b) lengthened, (c) kept unchanged, while its phase angle remains unchanged, to give $g_n(\vec{r}_j)$ whose magnitude equals $|f(\vec{r}_j)|$.

The correct complex amplitudes. In equation form, Gerchberg-Saxton algorithm can be written, for the $n^{th}$ iteration, as:

$$
\{g_n(\vec{r})\} = \{|g_n(\vec{r})| \exp(i\theta_n(\vec{r}))\} = FT^{-1}(\{G_n(\vec{q})\}) , \quad (2.3)
$$

$$
\{f(\vec{r})\} = \{|f(\vec{r})| \exp(i\theta_n(\vec{r}))\} , \quad (2.4)
$$

$$
\{G_n(\vec{q})\} = \{|G_n(\vec{q})| \exp(i\phi_n(\vec{q}))\} = FT(\{g_n(\vec{r})\}) , \quad (2.5)
$$

$$
\{G_{n+1}(\vec{q})\} = \{|F(\vec{q})| \exp(i\phi_n(\vec{q}))\} . \quad (2.6)
$$

The sums of squared errors:

$$
E_{F,n}^2 = N^{-1} \sum_{\vec{q}} |\Delta G_{\vec{q},n}|^2 = N^{-1} \sum_{\vec{q}} |G_{\vec{q},n+1} - G_{\vec{q},n}|^2 \quad (2.7)
$$

$$
E_{0,n}^2 = \sum_j |\Delta g_n(\vec{r}_j)|^2 = \sum_j |g_n(\vec{r}_j) - g_n(\vec{r}_j)|^2 \quad (2.8)
$$

measure, respectively, the degrees of constraint violation in diffraction and object domains in the $n^{th}$ iteration, and can be used to monitor convergence of the Gerchberg-
Saxton algorithm. When either one of these goes to zero, so does the other one, and we have found the pair of functions \( \{ \tilde{G}(\vec{q}) \} \) and \( \{ \tilde{g}(\vec{r}) \} = FT^{-1}(\{ \tilde{G}(\vec{q}) \}) \) that respectively satisfies constraints in diffraction and object domains. We will now show that \( E_{F,n}^2 \) and \( E_{0,n}^2 \) must not increase with each pass through the Gerchberg-Saxton loop.

Step (b) of the Gerchberg-Saxton algorithm can be written as:

\[
\{ g_n'(\vec{r}) \} + \{ \Delta g_n(\vec{r}) \} = \{ g_n(\vec{r}) \}. \tag{2.9}
\]

Apply Fourier transforms to both sides of Eq. (2.9) and look at the triangle inequality\(^\text{2}\) for a particular \( \vec{q} \):

\[
\{ G_{\vec{q},n}(\vec{q}) \} + FT(\{ \Delta g_n(\vec{r}) \}) = \{ G_n(\vec{q}) \}, \tag{2.10}
\]

\[
G_{\vec{q},n} + FT(\{ \Delta g_n(\vec{r}) \})_{\vec{q}} = G_{\vec{q},n}, \tag{2.11}
\]

\[
|FT(\{ \Delta g_n(\vec{r}) \})_{\vec{q}}| \geq ||G_{\vec{q},n'} - |G_{\vec{q},n}||. \tag{2.12}
\]

Noting that \( G_{\vec{q},n} \) and \( G_{\vec{q},n+1} \) both satisfy the diffraction-domain constraints for \( \vec{q} \) and thus have the same magnitude, and that \( G_{\vec{q},n+1} \) and \( G_{\vec{q},n} \) have the same phase angle (\( G_{\vec{q},n+1} \) is the magnitude-adjusted version of \( G_{\vec{q},n} \)) RHS of Eq. (2.12) becomes

\[
||G_{\vec{q},n'} - |G_{\vec{q},n}|| = ||G_{\vec{q},n+1} - |G_{\vec{q},n}||, \tag{2.13}
\]

\[
= |G_{\vec{q},n+1} - G_{\vec{q},n}|, \tag{2.14}
\]

\[
= |\Delta G_{\vec{q},n}|. \tag{2.15}
\]

\(^\text{2}\)If \( \mathbf{a} + \mathbf{b} = \mathbf{c} \), then \( |\mathbf{b}| \geq |||\mathbf{a}| - |\mathbf{c}|| \) where \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \) are either vectors or complex numbers.
and we have

\[ |FT(\{\Delta g_n(\vec{r})\})_{\vec{q}}| \geq |\Delta G_{\vec{q},n}|. \]  

(2.16)

Square both sides, then sum over \(\vec{q}\):

\[ \sum_{\vec{q}} |FT(\{\Delta g_n(\vec{r})\})_{\vec{q}}|^2 \geq \sum_{\vec{q}} |\Delta G_{\vec{q},n}|^2. \]  

(2.17)

Upon application of Parseval’s theorem,\(^3\) we obtain:

\[ N \sum_j |\Delta g_n(\vec{r}_j)|^2 \geq \sum_{\vec{q}} |\Delta G_{\vec{q},n}|^2, \]  

(2.18)

or

\[ E_{0,n}^2 \geq E_{F,n}^2. \]  

(2.19)

Similarly, step (d) of the Gerchberg-Saxton algorithm can be written as:

\[ \{G_n(\vec{q})\} + \{\Delta G_n(\vec{q})\} = \{G_{n+1}(\vec{q})\}. \]  

(2.20)

Apply inverse Fourier transforms to both sides of Eq. (2.20) and look at the triangle inequality for a particular \(\vec{r}\):

\[ \{g_n(\vec{r})\} + FT^{-1}(\{\Delta G_n(\vec{q})\}) = \{g_{n+1}(\vec{r})\}, \]  

(2.21)

\(^3\)Parseval’s theorem: For the Fourier transform pair \(\{H(\vec{q})\} = FT(\{h(\vec{r})\}),\)

\[ |H_{\vec{q}}|^2 = \sum_{j,k} h(\vec{r}_j)h^*(\vec{r}_k) \exp(2\pi i \vec{q} \cdot (\vec{r}_j - \vec{r}_k)), \]

\[ \sum_{\vec{q}} |H_{\vec{q}}|^2 = \sum_{j,k} h(\vec{r}_j)h^*(\vec{r}_k)N \delta_{j,k} = N \sum_j |h(\vec{r}_j)|^2, \]

\[ N \sum_j |h(\vec{r}_j)|^2 = \sum_{\vec{q}} |H_{\vec{q}}|^2 = \sum_{\vec{q}} |FT^{-1}(\{H(\vec{q})\})_{\vec{r}}|^2 = \sum_{\vec{q}} |FT(\{h(\vec{r})\})_{\vec{q}}|^2. \]
\[ g_n(\vec{r}_j) + FT^{-1}(\{\Delta G_n(\vec{q})\})_{\vec{r}_j} = g'_{n+1}(\vec{r}_j), \tag{2.22} \]

\[ |FT^{-1}(\{\Delta G_n(\vec{q})\})_{\vec{r}_j}| \geq ||g_n(\vec{r}_j)| - |g'_{n+1}(\vec{r}_j)||. \tag{2.23} \]

Noting that \(g_n(\vec{r}_j)\) and \(g_{n+1}(\vec{r}_j)\) both satisfy the object-domain constraints for \(\vec{r}_j\) and thus have the same magnitude, and that \(g_{n+1}(\vec{r}_j)\) and \(g'_{n+1}(\vec{r}_j)\) have the same phase angle \((g_{n+1}(\vec{r}_j)\) is the magnitude-adjusted version of \(g'_{n+1}(\vec{r}_j)\),) RHS of Eq. (2.23) becomes

\[ ||g_n(\vec{r}_j)| - |g'_{n+1}(\vec{r}_j)|| = ||g_{n+1}(\vec{r}_j)| - |g'_{n+1}(\vec{r}_j)||, \tag{2.24} \]

\[ = |g_{n+1}(\vec{r}_j) - g'_{n+1}(\vec{r}_j)|, \tag{2.25} \]

\[ = |\Delta g_{n+1}(\vec{r}_j)|, \tag{2.26} \]

and we have

\[ |FT^{-1}(\{\Delta G_n(\vec{q})\})_{\vec{r}_j}| \geq |\Delta g_{n+1}(\vec{r}_j)|. \tag{2.27} \]

Square both sides, then sum over \(j\):

\[ \sum_j |FT^{-1}(\{\Delta G_n(\vec{q})\})_{\vec{r}_j}|^2 \geq \sum_j |\Delta g_{n+1}(\vec{r}_j)|^2. \tag{2.28} \]

Upon application of Parseval’s theorem, we obtain:

\[ N^{-1} \sum_{\vec{q}} |\Delta G_{\vec{q},n}|^2 \geq \sum_j |\Delta g_{n+1}(\vec{r}_j)|^2, \tag{2.29} \]

or

\[ E_{F,n}^2 \geq E_{\tilde{q},n+1}^2. \tag{2.30} \]
Combining Eqs. (2.19) and (2.30), we arrive at

\[ E_{0,n}^2 \geq E_{F,n}^2 \geq E_{0,n+1}^2 \geq E_{F,n+1}^2, \]  

(2.31)

which states that the sum of squared errors in both diffraction and object domains must not increase with each pass through the Gerchberg-Saxton loop, or in other words, Gerchberg-Saxton algorithm converges.

The original algorithm of Gerchberg and Saxton only applies to problems where intensities are measured in both diffraction and object planes. The authors, however, had the foresight to suggest that their algorithm “may have exciting implications for crystallography where only the X-ray diffraction pattern may be measured.”

2.2.2 Object-Domain Constraints and Object-Domain Operations

The Gerchberg-Saxton algorithm, as described in the last section, cannot be applied to x-ray diffraction where only diffraction intensities are accessible. It must be generalized to allow other types of constraints or a priori knowledge to be enforced in the object domain.

Fienup modified the Gerchberg-Saxton algorithm in 1978 for use in problems where intensities in only diffraction space are accessible. The Fienup algorithm is identical to that of Gerchberg-Saxton except in object space, where no intensity information is available, constraints such as positivity (i.e. object wave function must be nonnegative) or rigid supports (i.e. object wave function is nonzero only inside certain regions) are imposed. When one or more of these object-domain constraints
are violated, a new wave function, that conforms to object-domain constraints, is
generated using what are referred to as object-domain operations. Four such opera-
tions were proposed, and iteration schemes using them were shown to have different
convergence properties (Fienup 1978, Fienup 1982). In particular, the error-reduction
operation was shown to be equivalent to a steepest descent gradient search.

In the error-reduction operation, one truncates the object wave function at places
where object-domain constraints are violated:

\[
g_n(\vec{r}) = \begin{cases} 
g'_n(\vec{r}) & , \{\vec{r}\} \notin \gamma \\
0 & , \{\vec{r}\} \in \gamma 
\end{cases}
\]  

(2.32)

Here the region \( \gamma \) includes all points at which \( g'_n(\vec{r}) \) violates the constraints. Figs. 2.4
and 2.5 show respectively how this is done in one dimension if positivity and rigid
supports are used as our object-domain constraints.

Figure 2.4 Error reduction (positivity) in 1D. \( g(x) \) is obtained from \( g'(x) \) by zeroing out
the negative parts.

The Fienup algorithm with error reduction can be shown to converge once we rec-
ognize that both error reduction and the magnitude-adjustment operation described
in the previous section (Figs. 2.2 and 2.3) apply the minimum change, as measured
Figure 2.5 Error reduction (rigid supports) in 1D. $g(x)$ is obtained from $g'(x)$ by truncating the parts that lie outside the support region.

by the sums of squared errors (Eqs. 2.7 and 2.8), to the object/ diffraction wave functions to make them conform to their respective constraints. It should be obvious from Figs. 2.4 and 2.5 that error reduction is such a minimum-change operation. Fig. 2.6 shows that this is also the case for the magnitude-adjustment operation when object/ diffraction intensities are available.

Fig. 2.7 shows a modified Gerchberg-Saxton loop in which changes applied to the object and diffraction wave functions are the minimum required to make them conform to their respective constraints. It is easy to show that algorithms based on this loop is guaranteed to converge.

In step (b) of the modified loop, both $g_n(\vec{r}_j)$ and $g_{n+1}(\vec{r}_j)$ satisfy the object-domain constraints for $\vec{r}_j$, but since $g_{n+1}(\vec{r}_j)$ is obtained from $g'_{n+1}(\vec{r}_j)$ through a minimum-change operation, we must have

$$\sum_j |g'_{n+1}(\vec{r}_j) - g_{n+1}(\vec{r}_j)|^2 \leq \sum_j |g'_{n+1}(\vec{r}_j) - g_n(\vec{r}_j)|^2. \quad (2.33)$$

Using Eq. (2.33) and Parseval’s theorem, the sum of squared errors in diffraction domain in the $n^{th}$ iteration must not be smaller than that in object domain in the
Figure 2.6 Schematics showing magnitude adjustment to be a minimum-change operation. (a) $|G_{q,n}| > |F_q|$. (b) $|G_{q,n}| < |F_q|$. Comparing the first row with the second row, it is obvious that magnitude of the change $\Delta G_{q,n}$ to make $G_{q,n}$ conform to the diffraction-domain constraint is minimized when $\Delta G_{q,n} \parallel G_{q,n}$. 
Figure 2.7 Schematic flowchart of a modified Gerchberg-Saxton loop. Minimum changes are applied to the wave functions in steps (b) and (d) to satisfy object- and diffraction-domain constraints respectively.

\[ n + 1^{st} \text{ iteration:} \]

\[
E_{F,n}^2 = N^{-1} \sum_{\vec{q}} |G_{\vec{q},n+1} - G_{\vec{q},n}|^2, \tag{2.34}
\]

\[
= \sum_j |g'_{n+1}(\vec{r}_j) - g_n(\vec{r}_j)|^2, \tag{2.35}
\]

\[
\geq \sum_j |g'_{n+1}(\vec{r}_j) - g_{n+1}(\vec{r}_j)|^2 = E_{0,n+1}^2, \tag{2.36}
\]

\[
E_{F,n}^2 \geq E_{0,n+1}^2. \tag{2.37}
\]

Similarly, both \( G_{\vec{q},n} \) and \( G_{\vec{q},n+1} \) satisfy the diffraction-domain constraints for \( \vec{q} \) in step (d), but since \( G_{\vec{q},n+1} \) is obtained from \( G_{\vec{q},n} \) through a minimum-change
operation, we must have

\[ N^{-1} \sum_{\vec{q}} |G_{\vec{q},n} - G_{\vec{q},n+1}|^2 \leq N^{-1} \sum_{\vec{q}} |G_{\vec{q},n} - G_{\vec{q},n}|^2. \]  

(2.38)

Using Eq. (2.38) and Parseval’s theorem, the sum of squared errors in object domain in the \( n^{th} \) iteration must not be smaller than that in diffraction domain in the \( n^{th} \) iteration:

\[
E_{0,n}^2 = \sum_j |g_n(\vec{r}_j) - g_{t_n}(\vec{r}_j)|^2, \tag{2.39}
\]

\[
= N^{-1} \sum_{\vec{q}} |G_{\vec{q},n} - G_{\vec{q},n}|^2, \tag{2.40}
\]

\[
\geq N^{-1} \sum_{\vec{q}} |G_{\vec{q},n} - G_{\vec{q},n+1}|^2 = E_{F,n}^2, \tag{2.41}
\]

\[
E_{0,n}^2 \geq E_{F,n}^2. \tag{2.42}
\]

Combining Eqs. (2.37) and (2.42), we arrive at

\[
E_{0,n}^2 \geq E_{F,n}^2 \geq E_{0,n+1}^2 \geq E_{F,n+1}^2, \tag{2.43}
\]

which states that the sums of squared errors in both diffraction and object domains must not increase with each pass through the modified Gerchberg-Saxton loop, or in other words, Fienup algorithm with error reduction converges. It is for this reason that we have chosen error reduction to be the object-domain operation in our direct-method algorithm.

For completeness, the other object-domain operations proposed by Fienup are listed below.
Input-output operation:

\[ g_n(\vec{r}) = \begin{cases} 
  g_{n-1}(\vec{r}) & , \{\vec{r}\} \notin \gamma \\
  g_{n-1}(\vec{r}) - \beta g'_n(\vec{r}) & , \{\vec{r}\} \in \gamma
\end{cases}. \quad (2.44) \]

Output-output operation:

\[ g_n(\vec{r}) = \begin{cases} 
  g'_n(\vec{r}) & , \{\vec{r}\} \notin \gamma \\
  g'_n(\vec{r}) - \beta g'_n(\vec{r}) & , \{\vec{r}\} \in \gamma
\end{cases}. \quad (2.45) \]

Hybrid input-output operation:

\[ g_n(\vec{r}) = \begin{cases} 
  g'_n(\vec{r}) & , \{\vec{r}\} \notin \gamma \\
  g_n(\vec{r}) - \beta g'_n(\vec{r}) & , \{\vec{r}\} \in \gamma
\end{cases}. \quad (2.46) \]

In Eqs. (2.44), (2.45) and (2.46), the region \( \gamma \) includes all points at which \( g'_n(\vec{r}) \) violates the constraints, and \( \beta \) is a parameter to be chosen either through trial-and-error or by experience.

2.2.3 Oversampling

The Fourier transform \( U(q) \) of a 1D continuous object function \( u(x) \) is given by:

\[ U(q) = \int_{-\infty}^{\infty} u(x) \exp(2\pi i q x) dx. \quad (2.47) \]
For the object function:

$$u_1(x) = \begin{cases} A , & |x| < a \\ 0 , & |x| > a \end{cases}$$

we have

$$U_1(q) = A \int_{-a}^{a} \exp(2\pi iqx) dx,$$

$$= \begin{cases} A \left[ \frac{\exp(2\pi iqx)}{2\pi i q} \right]_{-a}^{a} , & q \neq 0 \\ A[x]_{-a}^{a} , & q = 0 \end{cases},$$

$$= \begin{cases} A \frac{\sin(2\pi qa)}{\pi q} , & q \neq 0 \\ 2aA , & q = 0 \end{cases},$$

$$= 2aA \sin(2qa)$$

where

$$\text{sinc}(\xi) \equiv \frac{\sin(\pi \xi)}{\pi \xi},$$

and

$$\text{sinc}(m - n) = \delta_{m,n}$$

for integers $m$ and $n$.

Any arbitrary 1D object function $u_2(x)$ that is nonzero only in the interval $(-a, a)$

---

4Most of the examples and proofs presented in this section are for 1D functions. This is purely for clarity and simplicity. The conclusions derived from these examples and proofs extend readily to functions of higher dimensions.
can be written as:

\[ u_2(x) = \begin{cases} 
   \sum_{n=-\infty}^{\infty} A_n \exp(-2\pi i q_n x), & |x| < a \\
   0, & |x| > a 
\end{cases} \]  

and its Fourier transform is given by

\[ U_2(q) = \sum_{n=-\infty}^{\infty} A_n \int_{-a}^{a} \exp[2\pi i (q - q_n)x] dx, \]

\[ = 2a \sum_{n=-\infty}^{\infty} A_n \text{sinc}[2a(q - q_n)]. \]  

(2.53)

Since \( u_2(x) \) is zero for \( |x| > a \), a consequence of the sampling theorem is that \( U_2(q) \) is completely determined if it is sampled at

\[ q_n = n\Delta, \quad -\infty < n < \infty \]  

(2.54)

where

\[ \Delta = \frac{1}{2a} \]  

(2.55)

is the sampling interval.\(^5\) This is called critical sampling.\(^6\)

With critical sampling and using Eq. (2.51), Eq. (2.53) gives, for \( q = q_m \),

\[ U_{2,m} = U_2(q_m) = 2a \sum_{n=-\infty}^{\infty} A_n \text{sinc}[2a\left(\frac{m}{2a} - \frac{n}{2a}\right)] = 2a \sum_{n=-\infty}^{\infty} A_n \delta_{m,n} = 2aA_m. \]  

(2.56)

Finally, we arrive at the expression

\[ U_2(q) = \sum_{n=-\infty}^{\infty} U_{2,n} \text{sinc}[2a(q - n\Delta)] \]  

(2.57)

\(^5\)Similarly, since \( u_1(x) \) is zero for \( |x| > a \), \( U_1(q) \) is completely determined if sampled at \( q_n = n\Delta = \frac{n\Delta}{2a} \).

\(^6\)\( a = \frac{1}{2\Delta} \) is called the Nyquist critical frequency.
which reconstructs the full function $U_2(q)$ from its samples $U_{2,n}$ at $q = n\Delta = \frac{n}{2a}$.

Critical sampling of a bandwidth-limited function thus allows it to be completely determined. The function’s Fourier counterpart, in this case the object function $u_2(x)$, can subsequently be recovered.

Since $U_2(q)$ is a continuous function, it can be sampled at intervals finer than $\Delta = \frac{1}{2a}$. However, there is no advantage in doing such oversampling since $U_2(q)$ can be completely determined with just the critical set of samples. For instance, the same object function $u_2(x)$ will be recovered whether $U_2(q)$ is sampled at $q = n\Delta$ (critical sampling) or $q = n\frac{\Delta}{2}$ (oversampling.) This requires, of course, that $U_2(q)$ be sampled as a complex quantity. When only the magnitudes of $U_2(q)$ are available, half the information is effectively gone, and twice as many samples must be collected just to regain the same amount of information. Some kind of iteration scheme is usually needed to recover either $U_2(q)$ or $u_2(x)$ from this set of oversampled magnitudes.

An oversampled set of magnitudes, combined with trial phases, corresponds, in general, to a critical set of samples for an object function with a bigger nonzero region. For instance, magnitudes of $U_2(q)$ at $q = n\frac{\Delta}{2}$, combined with trial phases, is, in general, a critical set of samples for a function $u'_2(x)$ whose nonzero region is twice as big as that of $u_2(x)$. Only when combined with the correct set of phases will this set of oversampled magnitudes correspond to an object function with a nonzero region of the expected size. Rigid supports (Fig. 2.5) is therefore a natural object-domain constraint to enforce while applying the Fienup algorithm on an oversampled set of diffraction magnitudes. By truncating the object function outside its expected extent in the object-domain operation of the Fienup algorithm, a very powerful negative-
feedback mechanism is set up that drives the trial phases towards the correct ones.

This idea was first pursued experimentally by Miao et al. in 1999. They oversampled the diffuse and continuous x-ray diffraction pattern of a non-crystalline 2D specimen (an array of gold dots deposited on a silicon nitride membrane to form a set of letters,) then, using their knowledge of the specimen’s dimensions, successfully recovered its structure using Fienup algorithm with rigid supports.

We will now turn to periodic functions and show how their Fourier transforms can be sampled to recover the underlying repeating units.

Specifically, we form the periodic function $u_3(x)$ using the $(-a, a)$ interval of $u_2(x)$ (Eq. 2.52) as the repeating unit:

$$u_3(x) = \begin{cases} 
\vdots \\
\sum_{n=-\infty}^{\infty} A_n \exp[-2\pi i q_n (x + 2a)] , & -3a < x < -a \\
\sum_{n=-\infty}^{\infty} A_n \exp(-2\pi i q_n x) , & -a < x < a \\
\sum_{n=-\infty}^{\infty} A_n \exp[-2\pi i q_n (x - 2a)] , & a < x < 3a \\
\vdots \\
\sum_{n=-\infty}^{\infty} A_n \exp[-2\pi i q_n (x - 2ta)] , & (2t - 1)a < x < (2t + 1)a \\
\vdots 
\end{cases} \quad (2.58)$$
Fourier transform of this function is given by:

\[ U_3(q) = \ldots \]

\[ + \exp(-2\pi i q 2a) \sum_{n=-\infty}^{\infty} A_n \int_{-3a}^{-a} \exp \left[ 2\pi i (q - q_n)(x + 2a) \right] dx \]

\[ + \sum_{n=-\infty}^{\infty} A_n \int_{-a}^{a} \exp \left[ 2\pi i (q - q_n)x \right] dx \]

\[ + \exp(2\pi i q 2a) \sum_{n=-\infty}^{\infty} A_n \int_{3a}^{a} \exp \left[ 2\pi i (q - q_n)(x - 2a) \right] dx \]

\[ + \ldots \] (2.59)

\[ + \exp(2\pi i q 2ta) \sum_{n=-\infty}^{\infty} A_n \int_{(2t-1)a}^{(2t+1)a} \exp \left[ 2\pi i (q - q_n)(x - 2ta) \right] dx \]

\[ + \ldots, \]

\[ = \ldots + e^{-2\pi i q 2a} + 1 + e^{2\pi i q 2a} + \ldots + e^{2\pi i q 2ta} + \ldots \]

\[ \times 2a \sum_{n=-\infty}^{\infty} A_n \text{sinc} \left[ 2a(q - q_n) \right]. \]

The last result is obtained after recognizing that all the integrals are the same as the one in Eq. (2.53) with the appropriate change of variables.

The factor \((\ldots + e^{-2\pi i q 2a} + 1 + e^{2\pi i q 2a} + \ldots + e^{2\pi i q 2ta} + \ldots)\) in Eq. (2.59), being the sum of many many complex numbers with unit moduli and phases uniformly distributed in \([0, 2\pi]\), is zero unless \(q = q_m = m\Delta = \frac{m}{2a}\), in which case it becomes equal to the total number of terms in the sum:

\[ (\ldots + e^{-2\pi i q 2a} + 1 + e^{2\pi i q 2a} + \ldots + e^{2\pi i q 2ta} + \ldots) = N \sum_{m=-\infty}^{\infty} \delta_{q,q_m}. \]

(2.60)

Using Eqs. (2.60), (2.51) and (2.56), Eq. (2.59) becomes:

\[ U_3(q) = N \sum_{m=-\infty}^{\infty} \delta_{q,q_m} 2a \sum_{n=-\infty}^{\infty} A_n \text{sinc} \left[ 2a(q - q_n) \right], \]

\[ = N \sum_{m=-\infty}^{\infty} \delta_{q,q_m} 2a \sum_{n=-\infty}^{\infty} A_n \delta_{m,n}, \]
\[ = N \sum_{m=-\infty}^{\infty} \delta_{q,q_m} 2aA_m, \]
\[ = N \sum_{m=-\infty}^{\infty} \delta_{q,q_m} U_{2,m}. \] 

(2.61)

The last result states that \( U_3(q) \) is a discrete function and consists of all the critical samples of \( U_2(q) \) (scaled by a constant \( N \).) Sampling all the “spikes” of \( U_3(q) \) thus allows \( U_2(q) \) to be completely determined. The underlying repeating unit in \( u_3(x) \), i.e. \( u_2(x) \), can be subsequently recovered.

This result can be readily extended to 3D. Consider a function that is periodic in all three Cartesian directions, and whose repeating unit has dimensions \( a_1, a_2 \) and \( a_3 \) in the x-, y- and z-directions respectively. Fourier transform of this function is discrete and consists of all the critical samples, at

\[ \vec{q} = \left( \frac{h}{a_1}, \frac{k}{a_2}, \frac{l}{a_3} \right), \] 

(2.62)

where \( h, k, l \) are integers, that are required to completely determine the repeating unit.

In bulk x-ray crystallography, where the electron density in a bulk specimen is a periodic function in 3D, scattering amplitudes (magnitudes and phases) with integer Laue indices (the so-called Bragg spots) form the set of critical samples that is required to completely determine the electron density in a bulk unit cell. In particular, when the unit cell is orthorhombic\(^7\) and has dimensions \( a_1, a_2 \) and \( a_3 \) in the x-, y- and z-directions respectively, the set of critical samples is given by Eq. (2.62) with integers \( h, k \) and \( l \).

\(^7\)A unit cell is orthorhombic if its three basis vectors are mutually orthogonal.
The lack of measured phases means, of course, that this set of critical samples of magnitudes cannot be used directly to reveal the content of a bulk unit cell. Since oversampling is not possible in this case, other sources of information must be sought. In some cases, knowledge of part of the structure has been used to help recover the unknown portion.\textsuperscript{8} Anomalous diffraction intensities from more than one x-ray wavelength have been used beneficially in other cases.\textsuperscript{9} These techniques are beyond the scope of this dissertation.

In surface x-ray diffraction, sometimes the surface reconstructs so that the dimensions of its 2D unit cell are larger than those of the bulk, in which case nonzero diffraction intensities can be measured for certain momentum transfer vectors with noninteger values of either or both of the in-plane Laue indices $h$ and $k$. It is important to realize that sampling these fractional order rods does not constitute oversampling. In fact, these rods must be sampled to give the critical sample set for the now bigger real space unit cell.

\section*{2.3 Our Direct-Method Algorithm for Surface X-Ray Diffraction}

While the work of both Fienup and Miao et al. concerned mostly with non-periodic 2D objects, their ideas can be readily applied in the realm of surface x-ray crystallography. In a nutshell, our direct-method algorithm for surface x-ray

\textsuperscript{8}This technique is known as structure completion. See Shneerson (2001) for details.

\textsuperscript{9}This technique is known as multiwavelength anomalous diffraction, or MAD. See Drenth (1995) and Rhodes (1993) for details.
diffraction (SXRD) (Saldin et al. 2001b, Saldin et al. 2002, Lyman et al. 2005) is
a 3D version of Fienup’s adaptation of the basic Gerchberg-Saxton algorithm that
also combines a structure completion feature for the CTRs where a knowledge of the
bulk structure is exploited. Oversampling of diffraction intensities is done along the
$\vec{b}_3$ direction in reciprocal space (corresponding to the non-periodic $\vec{a}_3$ direction in real
space,) allowing application of error reduction when the rigid-supports constraint is
violated.

In the technique of SXRD, x-rays are generally incident on a surface at a glancing
angle to enhance the sensitivity to the scattered signal from the surface region. In the
case of a surface with a different in-plane (parallel to surface) periodicity from that
of the bulk, the intensities of the superstructure reflections will contain information
from just that surface region. The integer-order reflections will have contributions
from both the surface and the bulk structure. Our direct-method algorithm exploits
the fact that the bulk structure is usually known, and bulk structure factors may be
calculated from this a priori knowledge.

The second peculiar feature of SXRD that we exploit is the fact that a surface
breaks the 3D periodicity of a bulk crystal in the direction normal to the surface.
Consequently, the intensities of all reflections are continuous in this direction. In the
usual nomenclature, the integer-order and fractional-order reflections are broadenend
into rods in reciprocal space normal to the surface, known as crystal truncation rods
(CTRs), and superstructure rods (SRs), respectively. Bearing in mind that the aim
of SXRD is to determine the structure of a thin slab of material near the surface,
it is possible to oversample the Fourier transform of its electron density distribution
in a direction normal to the surface. This allows the application of an iterative computer algorithm that imposes a constraint of compact support on the electron density distribution in a direction normal to the surface, analogous to the methods developed by Miao et al. for non-periodic objects in order to determine the phases of the measured reflections.

Figure 2.8 Schematic flowchart of iterative phase recovery algorithm.

In each cycle of our direct-method algorithm (Fig. 2.8), electron densities for grid points outside the expected extent of the surface region (i.e. \( \{ \vec{r} \} \in \gamma \)) are truncated in real space:

\[
\{ u^{(n)} \} = \begin{cases} 
\{ t^{(n)} \} , & \{ \vec{r} \} \notin \gamma \\
0 , & \{ \vec{r} \} \in \gamma 
\end{cases}
\]  
(2.63)

The Fourier transform of these updated surface electron densities gives the surface
contributions \( \{S\} \) to the structure factors:

\[
\{S_{\text{calc}}^{(n+1)}\} = FT(\{u^{(n)}\}).
\]  

(2.64)

Adding the contributions \( \{B\} \) of the bulk to these structure factors, results in total scattering amplitudes with updated phases:

\[
\{\phi_{\text{calc}}^{(n+1)}\} = \text{arg}(\{B + S_{\text{calc}}^{(n+1)}\}).
\]  

(2.65)

The magnitudes of these total structure factors are now assigned values determined from experiment. Combining the assigned phases (Eq. (2.65)) with these experimental structure factor amplitudes gives new estimates of the experimental structure factors:

\[
\{F^{(n+1)}\} = \{|F_{\text{obs}}| \exp(i\phi_{\text{calc}}^{(n+1)})\}
\]  

(2.66)

from which the bulk contributions are subtracted. An inverse Fourier transform

\[
\{u^{(n+1)}\} = FT^{-1}(\{F^{(n+1)} - B\})
\]  

(2.67)

of the updated surface structure factors gives a new estimate of the surface electron density (Eq. (2.67)) that satisfies the reciprocal-space constraints of measured structure-factor amplitudes, and the entire cycle is repeated.

On starting with a random or flat distribution of electron densities \( \{u^{(0)}\} \) in real space (Eq. (2.64)), or a random set of phases \( \{\phi^{(1)}\} \) in reciprocal space (Eq. (2.66)), our algorithm usually converges within a few tens of iterations to give a clean image showing concentrations of electron densities, which may be interpreted to give a starting surface model for conventional refinement.
Our direct-method algorithm, as detailed above, has been successfully tested on a variety of realistic simulated experimental systems: O/Cu (104) (1 × 1) (with CTR reflections only) (Saldin et al. 2001b), GaAs (111) (2 × 2) (with both CTR and SR reflections) (Saldin et al. 2001b) and Ge (001) (2 × 1) (with both CTR and SR reflections, and with multiple domains) (Saldin et al. 2002).

More recently, on the experimental front, our direct-method algorithm has been applied on data from the well-known Au (110) (1 × 2) reconstruction (Lyman et al. 2005). Our results agree very well with models published in the literature. We have also applied our direct-method algorithm to determine the unknown structures of the c(2 × 2) and \( (\sqrt{3} \times \sqrt{3}) \) \( 54.7° \) reconstructions found in the Sb/ Au (110) system. These are the subjects of Chapters 5, 6 and 7.
Chapter 3

The Au(110) System

3.1 Au(110) and Choice of Basis Vectors

Gold (Au) crystallizes to form a face-centered cubic (fcc) structure (Fig. 3.1) with lattice parameter $a_{fcc} = 4.08\text{Å}$. Amongst the lowest-index faces of a fcc lattice (Fig. 3.2), the (110) face is the most open one (Fig. 3.3) and it is this face of Au that we have chosen to test our direct-method algorithm on.

In Surface X-Ray Diffraction (SXRD), real space basis vectors $\{\vec{a}\}$ are customarily chosen so that $\vec{a}_1$ and $\vec{a}_2$ are parallel to the surface of a sample, and $\vec{a}_3$ is normal to the surface. The conventional choice for the (110) face of fcc is the orthogonal set of
Figure 3.2 The three lowest-index surfaces of a fcc lattice: (100), (110) and (111).

Figure 3.3 A, B .. G are 2D unit cells that repeat to form atomic layers of a fcc lattice parallel to one of the three lowest-index faces (Fig. 3.2). Filled circles denote basis atoms while unfilled circles denote locations occupied by basis atoms of neighboring unit cells. The (100), (110) and (111) faces of fcc are generated respectively by the stacking sequences ABABA ..., CDCDC ... and EFGFGE ... The 2D atomic densities of the (100), (110) and (111) faces of fcc are respectively 2, 1.4 and 2.3 atoms per $a_{fcc}^2$ of area, where $a_{fcc}$ is the lattice parameter. The (110) face is therefore the most open low-index face of a fcc lattice.
vectors: \( \{ \vec{a}_1 = \frac{1}{2}(110)_{\text{cub}}, \vec{a}_2 = (001)_{\text{cub}}, \vec{a}_3 = \frac{1}{2}(110)_{\text{cub}} \} \), where the subscript refers to the conventional cubic unit cell. The unit cell formed by these vectors is shown in Fig. 3.4 together with the conventional fcc cubic unit cell. Dimensions of this unit cell are \( a_1 = a_3 = \frac{1}{\sqrt{2}} a_{\text{fcc}} \) and \( a_2 = a_{\text{fcc}} \) (for Au: \( a_1 = a_3 = 2.88\text{Å} \) and \( a_2 = 4.08\text{Å} \),) and its basis consists of identical atoms at \((0, 0, 0)\) and \((0.5, 0.5, 0.5)\) where the coordinates are expressed as fractions of the basis vectors \( \{ \vec{a} \} \). From now on we will refer to this unit cell as the Au(110) bulk unit cell, and the directions \( \hat{a}_1, \hat{a}_2 \) and \( \hat{a}_3 \) as x-, y- and z-directions respectively. It should be obvious, from Fig. 3.3, that the Au(110) bulk has \( p2mm \) symmetry.\(^1\) In reciprocal space, the corresponding basis vectors are \( \{ \vec{b}_1 = (T10)_{\text{cub}}, \vec{b}_2 = (001)_{\text{cub}}, \vec{b}_3 = (110)_{\text{cub}} \} \).

\[ z \\
[001] a_{\text{ge}} \\
[110] a_{\text{ge}} \\
[101] a_{\text{ge}} \]

\[ x \]

\[ y \]

\[ \vec{b}_1 = (T10)_{\text{cub}}, \vec{b}_2 = (001)_{\text{cub}}, \vec{b}_3 = (110)_{\text{cub}} \].

\[ 1 \text{To be more precise, the Au bulk has one mirror plane normal to the [001] direction and another one normal to the [T10] direction (Fig. 3.4). Therefore, looking down the [110] direction, the Au bulk has } p2mm \text{ symmetry.} \]

Figure 3.4  Au(110) bulk unit cell (or conventional unit cell for the (110) face of fcc) (thick outline) shown in relation to the conventional fcc cubic unit cell (thin outline.) Its basis consists of two atoms: one at one of the vertices (filled circles) and one at the body center (unfilled circle.)
3.2 Clean and Sb-covered Au(110)

The clean Au(110) face is known to undergo a \((1 \times 2)\) reconstruction (Copel and Gustafsson (1986), Moritz and Wolf (1985), Vlieg et al. (1990)). Major features of this reconstruction include the disappearance of every other row of Au atoms along the \([\mathbf{T}10]\) direction, top-layer contraction, second-layer expansion, second- and fourth-layer pairings, and third-layer buckling (Fig. 3.5). These features, which collectively constitute the so-called missing-row model, have been known or proposed by different researchers for many years. Using our direct-method algorithm, we were able to recover all these features with one set of experimental data. This work is described in Chapter 5.

When covered by Sb adatoms, the Au(110) face successively exhibits several different surface reconstructions. Using low energy electron diffraction (LEED), we have found a \(c(2 \times 2)\), a \(\left(\sqrt{3} \times \sqrt{3}\right) R54.7^\circ\), and a \(p(5 \times 6)\) phase at Sb coverages of about \(\frac{1}{2}\), \(\frac{2}{3}\) and \(> 1\) monolayers respectively. These phases have not been reported in the literature before. Subsequently, we measured SXRD data for these three phases. The use of our direct-method algorithm for the determination of the structures of the \(c(2 \times 2)\) and \(\left(\sqrt{3} \times \sqrt{3}\right) R54.7^\circ\) phases are described respectively in Chapters 6 and 7.
Figure 3.5 Sideview of the Au(110) system. (a) Bulk termination. (b) \((1\times2)\) reconstruction: Every other row of atoms along the \([\bar{1}10]\) direction is missing. Arrows indicate displacement of atoms from their bulk locations. Black, white and gray arrows denote respectively top-layer contraction, second- and fourth-layer pairings, and third-layer buckling. It is obvious from these schematics that the dimension of the reconstructed surface unit cell along the \(\vec{a}_2\) (i.e \([001]\)) direction is two times that of the bulk unit cell.
Chapter 4

Experimental Techniques and Reduction of Data

4.1 Obtaining Sb Coverage by X-ray Photoelectron Spectroscopy (XPS)

Here we provide a brief description of how XPS results have been used to determine the Sb coverage on our experimental systems. See Seah (1983) for more detailed discussions.

By definition, photoelectric cross-section $\sigma$ of a material is the number of photoelectrons given out by one atom (or molecule) of that material per unit time divided by the incident photon intensity:

$$\sigma = \frac{\# \text{ photoelectrons}}{\text{time} \times \# \text{ atoms}} / \frac{\# \text{ incident photons}}{\text{time} \times \text{area}}, \quad (4.1)$$

where the symbol $\#$ denotes “number of”. RHS of Eq. (4.1) can be rearranged to give

$$\sigma = \frac{\# \text{ photoelectrons per unit thickness}}{\# \text{ incident photons} / \text{volume}} = \frac{\Gamma}{\rho N_A}, \quad (4.2)$$

where $\rho$ and $M$ are respectively the mass density and the atomic (or molecular) mass of the material, and $N_A$ is the Avogadro constant. $\Gamma$ denotes the number of photoelectrons given out by a unit thickness of the material for each incident photon,
and is given by (Eq. (4.2)):

\[ \Gamma = \frac{\rho N_A \sigma}{M}. \]  \hspace{1cm} (4.3)

Consider photoelectrons coming out of a sample where a thickness \( t \) of material 2 has been deposited on top of a semi-infinite substrate of material 1 (Fig. 4.1).

![Figure 4.1 Schematic diagram of our sample consisting of an adlayer (material 2) of thickness \( t \) on top of a semi-infinite substrate (material 1.) A differential element of thickness \( dz \) is shown within the substrate region. Photoelectrons produced in this differential element have to go through thickness \( z - t \) of material 1 and thickness \( t \) of material 2 before they can be detected.](image)

Photoelectrons produced inside the sample suffer collisions on their way to the surface to be detected and are thus attenuated. In particular, photoelectrons produced in material R have an inelastic mean free path \( \lambda_{R,S} \) while traveling in material S, and are attenuated by the exponential factor \( \exp \left( -\frac{d}{\lambda_{R,S}} \right) \) after traveling through a distance \( d \) in material S.

A differential element of material 1 of thickness \( dz \) situated at a distance \( z \) below
the surface (Fig. 4.1) gives out, for each incident photon,

\[ dN_1 = \Gamma_1 dz \exp\left(-\frac{z-t}{\lambda_{1,1}}\right) \exp\left(-\frac{t}{\lambda_{1,2}}\right) \]  

(4.4)

photoelectrons (after attenuation.) Total number of photoelectrons coming out of the substrate (material 1,) for each incident photon, is therefore:

\[ N_1 = \int_{z=t}^{z=\infty} \Gamma_1 dz \exp\left(-\frac{z-t}{\lambda_{1,1}}\right) \exp\left(-\frac{t}{\lambda_{1,2}}\right), \]

\[ = \lambda_{1,1} \Gamma_1 \exp\left(-\frac{t}{\lambda_{1,2}}\right). \]  

(4.5)

Figure 4.2 Schematic diagram of our sample consisting of an adlayer (material 2) of thickness \( t \) on top of a semi-infinite substrate (material 1.) A differential element of thickness \( dz \) is shown within the adlayer region. Photoelectrons produced in this differential element have to go through thickness \( z \) of material 2 before they can be detected.

Similarly, total number of photoelectrons coming out of the adlayer (material 2) (Fig. 4.2), for each incident photon, is:

\[ N_2 = \int_{z=0}^{z=t} \Gamma_2 dz \exp\left(-\frac{z}{\lambda_{2,2}}\right), \]
\[ I_2 = \lambda_{2,2} \Gamma_2 \left[ 1 - \exp \left( -\frac{t}{\lambda_{2,2}} \right) \right] . \quad (4.6) \]

The ratio of the photoelectron intensities, \( I_2 / I_1 = N_2 / N_1 \), can be readily obtained in a XPS experiment. Material properties \( \lambda, \rho, \sigma \) and \( M \) (and hence \( \Gamma \)) can be looked up or calculated. The thickness \( t \) of the adlayer can therefore be obtained by solving the equation:

\[ \frac{I_2}{I_1} = \frac{\lambda_{2,2} \Gamma_2}{\lambda_{1,1} \Gamma_1} \frac{1 - \exp \left( -\frac{t}{\lambda_{2,2}} \right)}{\exp \left( -\frac{t}{\lambda_{1,2}} \right)}. \quad (4.7) \]

If we make the approximation \( \lambda_{1,2} \approx \lambda_{2,2} \) (i.e. inelastic mean free path of photoelectrons depends on where they travel but does not depend on where they are produced) and write \( \lambda_1 \equiv \lambda_{1,1} \) and \( \lambda_2 \equiv \lambda_{2,2} \), then

\[ \frac{I_2}{I_1} \approx \frac{\lambda_2 \Gamma_2}{\lambda_1 \Gamma_1} \left[ \exp \left( \frac{t}{\lambda_2} \right) - 1 \right], \quad (4.8) \]

or

\[ t \approx \lambda_2 \ln \left( \frac{I_2 \lambda_1 \Gamma_1}{I_1 \lambda_2 \Gamma_2} + 1 \right). \quad (4.9) \]

Taking materials 1 and 2 to be respectively Au and Sb, and using the values for material properties listed in Table 4.1, thickness of Sb adlayers \( t_{Sb} \) in our samples can be calculated using:

\[ t_{Sb} (\text{in } \text{Å}) \approx 19.3 \times \ln \left( \frac{I_{Sb}}{I_{Au}} \times 0.262 + 1 \right). \quad (4.10) \]

Finally, the Sb-coverage \( \theta_{Sb} \) is related to the thickness of the Sb-adlayer \( t_{Sb} \) through:

\[ \theta_{Sb} = \# \text{ Sb atoms} / \# \text{ surface sites}, \]
Table 4.1 Some material properties of Au and Sb. \( \rho \): mass density; \( M \): atomic mass; \( \sigma \): photoelectric cross-section (Cromer and Liberman (1970)); \( \lambda \): inelastic mean free path of electrons (Powell and Jablonski (2000)).

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Material} & \rho (g/m^3) & M (g/mol) & \sigma (10^{-28} m^2) & \lambda (\text{Å}) \\
\hline
\text{Au} & 1.932 \times 10^7 & 196.97 & 7.87 \times 10^4 & 13.16 \\
\text{Sb} & 6.684 \times 10^6 & 121.76 & 3.66 \times 10^5 & 19.29 \\
\hline
\end{array}
\]

4.2 Applying corrections to measured intensities

Fig. 4.3 is a schematic of our experimental system. The x-ray beam from the synchrotron is split into two by a beam splitter, one goes directly to a detector (monitor count \( M_i \)) while the other is diffracted off the sample before it is detected.
Figure 4.3 Schematic diagram of our experimental system. See main text for a description.

(diffraction count $C$.) Our measure of diffraction intensity is the reflectivity $R$, given by:

$$ R = \frac{C}{M}. $$

(4.13)

The intensity of x rays reaching the sample fluctuates over the course of the experiment; this fluctuation modulates the regular variation in diffraction intensity as a function of momentum transfer vector, which is what we want to measure. Dividing diffraction counts by their corresponding monitor counts removes this undesired modulation.

Uncertainties $\sigma$ in $R$, $C$ and $M$ are related through $^1$

$$ \left( \frac{\sigma_R}{R} \right)^2 = \left( \frac{\sigma_C}{C} \right)^2 + \left( \frac{\sigma_M}{M} \right)^2, $$

(4.14)

$^1$If uncorrelated variables $u$ and $v$ are sampled respectively from distributions with variances $\sigma_u^2$ and $\sigma_v^2$ to determine $x$ which is a function of these two variables, then the variance of $x$ is given by $\sigma_x^2 \approx \sigma_u^2 \left( \frac{\partial x}{\partial u} \right)^2 + \sigma_v^2 \left( \frac{\partial x}{\partial v} \right)^2$. In particular, if $x = \frac{u}{v}$, then $\frac{\sigma_x^2}{\sigma_x^2} = \frac{\sigma_u^2}{\sigma_x^2} + \frac{\sigma_v^2}{\sigma_x^2}$, or if $x = u \pm v$, then $\sigma_x^2 = \sigma_u^2 + \sigma_v^2$. 
or, using Eq. (4.13):

$$\sigma_R^2 = \left(\frac{C}{M}\right)^2 \left[\left(\frac{\sigma_C}{C}\right)^2 + \left(\frac{\sigma_M}{M}\right)^2\right].$$ (4.15)

X rays coming in at different angles are polarized differently, and are diffracted differently as a result. Diffracted x rays hitting the detector at different angles are spread out over different areas. X rays coming in and leaving the sample at different angles travel different distances in both real and reciprocal space. These and other geometric factors must be corrected for before the measured intensities can be used to solve for structures. Derivation of these geometric correction factors requires understanding of the detailed experimental setup, and is beyond the scope of this dissertation. See Vlieg (1997) for details.

Intensities of diffracted x rays vary over many orders of magnitudes. To measure them using detectors with limited range as well as to utilize as much as possible the most sensitive range of the detectors, attenuators (made of aluminum foil) are often used when measuring high diffraction intensities so that the number of x-ray photons hitting the detectors are kept under about ten thousand per second. Calculation of the attenuation factors of the individual attenuators is discussed in Appendix B.

If $\gamma$ is the overall correction factor:

$$\gamma = \text{attenuation correction} \times \text{geometric correction},$$ (4.16)

then the corrected diffraction count and the detected diffraction count and their

\[\text{Note that both attenuation and geometric corrections are generally different for each measured reflection.}\]
uncertainties are related through:

\[ C_{\text{corr}} = C_{\text{det}} / \gamma, \]  \hspace{1cm} (4.17)

\[ \sigma_{C_{\text{corr}}} = \sigma_{C_{\text{det}}} / \gamma. \]  \hspace{1cm} (4.18)

Counting (Poisson) Statistics applies here, therefore:

\[ \sigma_{C_{\text{det}}}^2 = C_{\text{det}}, \]  \hspace{1cm} (4.19)

\[ \sigma_{M}^2 = M. \]  \hspace{1cm} (4.20)

Using Eqs. (4.18), (4.19) and (4.17), we get:

\[ \sigma_{C_{\text{corr}}}^2 = \sigma_{C_{\text{det}}}^2 / \gamma^2 = C_{\text{det}} / \gamma^2 = C_{\text{corr}} / \gamma. \]  \hspace{1cm} (4.21)

Even though each momentum transfer vector \( \vec{q} = (h, k, l) \) corresponds to a point in diffraction space, diffraction intensities are not measured at isolated points in diffraction space. In fact, counts are taken over a small range of \( \vec{q} \) in the neighborhood of each momentum transfer vector of interest (Robinson 1991), and the resulting rocking curve (Fig. 4.4), which is a plot of the corrected reflectivity \( (R_{\text{corr}} = C_{\text{corr}} / M) \) as a function of \( \vec{q} \) (or equivalently the rocking angle,) is then fitted to separate the diffraction signal from the background. Diffraction signals usually have Lorentzian shapes and backgrounds usually have either Lorentzian or Gaussian shapes, depending on the region of diffraction space we are looking at.

After taking out the background, the area under the diffraction signal is integrated
Figure 4.4 A typical rocking curve. Left: Corrected reflectivities (circles) are plotted as a function of the rocking angle. The solid curve is the fitted background. Signal is the region between the two vertical lines above the background. Right: The area under the signal between the two vertical lines (shaded) is integrated to give the diffracted intensity.

and the result is taken as a measure of the diffraction intensity:

\[
I = \int R_S^{\text{corr}} \, d\theta = \int R_M^{\text{corr}} \, d\theta - \int R_B^{\text{corr}} \, d\theta,
\]

(4.22)

where the subscripts \( M \), \( S \) and \( B \) refer to Measured, Signal and Background respectively, and \( \theta \) is the rocking angle.

Uncertainty in diffracted intensity can be found by adding the uncertainties in measured and background reflectivities in quadrature:

\[
\sigma_I = \sqrt{\int \sigma_{R_M^{\text{corr}}}^2 \, d\theta + \int \sigma_{R_B^{\text{corr}}}^2 \, d\theta},
\]

(4.23)

Using Eqs. (4.15), (4.21), (4.20) and (4.17), this becomes:

\[
\sigma_I = \sqrt{\int d\theta \left\{ \left( \frac{C_M^{\text{corr}}}{M} \right)^2 \left[ \left( \frac{\sigma_{C_M^{\text{corr}}}}{C_M^{\text{corr}}} \right)^2 + \left( \frac{\sigma_M}{M} \right)^2 \right] + \left( \frac{C_B^{\text{corr}}}{M} \right)^2 \left[ \left( \frac{\sigma_{C_B^{\text{corr}}}}{C_B^{\text{corr}}} \right)^2 + \left( \frac{\sigma_B}{M} \right)^2 \right] \right\}},
\]

\[
= \sqrt{\int d\theta \left\{ \frac{1}{M^2} \left( \sigma_{C_M^{\text{corr}}}^2 + \sigma_{C_B^{\text{corr}}}^2 \right) + \frac{\sigma_M^2}{M^4} \left[ \left( C_M^{\text{corr}} \right)^2 + \left( C_B^{\text{corr}} \right)^2 \right] \right\}},
\]
\[
= \sqrt{\int d\theta \left\{ \frac{1}{M^2} \left( C_{M}^{corr} + C_{B}^{corr} \right) + \frac{1}{M^3} \left[ (C_{M}^{corr})^2 + (C_{B}^{corr})^2 \right] \right\} }, \tag{4.24}
\]
\[
= \frac{1}{\gamma} \sqrt{\int d\theta \left\{ \frac{1}{M^2} \left( C_{M}^{det} + C_{B}^{det} \right) + \frac{1}{M^3} \left[ (C_{M}^{det})^2 + (C_{B}^{det})^2 \right] \right\} }. \tag{4.25}
\]

### 4.3 Combining equivalent scans

Oftentimes it is desirable to measure more than once the intensity of each inequivalent reflection. This gives us a measure of the uncertainties in the determination of intensities of particular reflections as well as provides a means for us to assess the systematic error inherent in the experimental setup.

Robinson gave in 1991 a recipe to combine equivalent scans. If the intensity of the reflection \((hkl)\) (or its equivalents) has been measured \(n\) times with results \(\{I_{hkl,i} \pm \sigma_{hkl,i}, i = 1 \ldots n\}\), the weighted average of these measurements (weight = \(1/\sigma^2\)) is taken as the best estimate of the true intensity:

\[
\bar{I}_{hkl} = \left( \sum_{i=1}^{n} \frac{I_{hkl,i}}{\sigma_{hkl,i}^2} \right) / \left( \sum_{i=1}^{n} \frac{1}{\sigma_{hkl,i}^2} \right), \tag{4.25}
\]

with average uncertainty:

\[ \bar{\sigma}_{hkl} = \left( \sum_{i=1}^{n} \frac{1}{\sigma_{hkl,i}^2} \right)^{-\frac{1}{2}}, \tag{4.26} \]

and standard deviation:

\[ s_{hkl} = \sqrt{\left( \sum_{i=1}^{n} \frac{I_{hkl,i}^2}{\sigma_{hkl,i}^2} \right) / \left( \sum_{i=1}^{n} \frac{1}{\sigma_{hkl,i}^2} \right) - \bar{I}_{hkl}^2}. \tag{4.27} \]
The systematic error is given by

\[ \epsilon = \frac{1}{N} \sum_{\tilde{I}_{hkl} > 2\tilde{\sigma}_{hkl}} \frac{s_{hkl}}{\tilde{I}_{hkl}}, \quad (4.28) \]

where \( N \) is the number of reflections included in the sum. These are the reflections that are considered to be reliable \((\tilde{I}_{hkl} > 2\tilde{\sigma}_{hkl})\).

Best estimate of the uncertainty in \( \tilde{I}_{hkl} \) is obtained by combining the average uncertainty \( \tilde{\sigma}_{hkl} \) and the systematic error \( \epsilon \tilde{I}_{hkl} \) in quadrature:

\[ (\Delta \tilde{I}_{hkl})^2 = \tilde{\sigma}_{hkl}^2 + \epsilon^2 \tilde{I}_{hkl}^2. \quad (4.29) \]
Chapter 5

Clean Au(110) \((1 \times 2)\)

5.1 From Theory to Experiment

Having tested our direct-method algorithm (Fig. 2.8 and Eqs. (2.63) to (2.67)) on a variety of realistic simulated experimental systems (Saldin et al. 2001b, 2002), the stage was set to apply it to experimental data. The ideal test system should have geometry and symmetry that are easy to work with (orthorhombic, single-domain, with one or two mirror planes perhaps,) so that we could concentrate on the general aspects of the problem, and not be overwhelmed by the specifics of particular systems. It should also be a system that is both well known and be of general interest. As a proof-of-principle exercise, having something to compare our results against was very important. It would also be of interest to compare, amongst the various techniques that have been applied on the same system, the amounts of data required, the ease of analysis, the strengths and weaknesses of the techniques, and the precisions of the final results.

The clean Au(110) face is known to undergo a \((1 \times 2)\) reconstruction. It is a single-domain system. Both the surface unit cell and the bulk unit cell are orthorhombic and have \(p2mm\) symmetry. This reconstruction has been studied extensively over the last two decades with many different techniques (Copel and Gustafsson (1986), Moritz and Wolf (1985), Vlieg et al. (1990)). There is a general consensus that every other
row of Au atoms along the [110] direction is missing, that the top layer contracts and the second layer expands, that there might be some pairings in the second and fourth layers, and perhaps some buckling in the third layer, although results from different techniques disagree on the significance or degrees of the various features/displacements. Being a system that is well known and of general interest (Keane et al. (1991), Vilfan and Villain (1991), Hoss et al. (1992)), and with simple symmetry and geometry, the clean Au(110) (1×2) surface reconstruction fits all the criteria of an ideal test system for our direct-method algorithm.

Once we have decided on a test system, a lot of work then went into establishing the minimum set of diffraction data (i.e. ranges of h, k and l (Eq. (1.3))) and Δl (or equivalently, the amount of oversampling, Sec. 2.2.3) that would be needed for our direct-method algorithm to work. After many painstaking hours of simulations, it was determined that diffraction intensities would be measured for 0 ≤ h ≤ 4; 0 ≤ k ≤ 4; 0.13 ≤ l ≤ 1.82;\(^1\) and with Δl = 0.13.\(^2\)

5.2 Results and Discussions

Fig. 5.1 is a schematic diagram of the observed (1×2) diffraction pattern. Nonzero diffraction intensities were found along rods with in-plane Laue indices \(h = m\) and \(k = \frac{n}{2}\), where \(m\) and \(n\) are both integers. The diffraction intensities were observed to

\(^1\)Experimental considerations also played a role in our choice of \(l_{\text{max}} = 1.82\).
\(^2\)The same set of reflections was measured in our Sb/ Au(110) experiments.
have the same $p2mm$ symmetry as the projected Au(110) bulk.

The surface unit cell that is consistent with this diffraction pattern has the same
to the projected Au(110) bulk. length along the $[\overline{1}10]$ (or $\tilde{a}_1$) direction as the bulk unit cell but is two times longer
than the latter along the [001] (or $\tilde{a}_2$) direction.

![Schematic diagram of our observed diffraction pattern. Filled and unfilled circles denote crystal-truncation-rod (CTR) and superstructure-rod (SR) reflections respectively.](image)

Fig. 5.1 Schematic diagram of our observed diffraction pattern. Filled and unfilled circles denote crystal-truncation-rod (CTR) and superstructure-rod (SR) reflections respectively.

Fig. 5.2 shows the autocorrelation map calculated with all the measured super-
structure intensities. Since we already knew roughly what the surface structure should
be, we did not need the autocorrelation map for model building. It has been used in-
stead to establish the vertical extent of the surface layer ($\sim 8\text{Å}$) and thus the support
constraint in the object-domain operation of our direct-method algorithm.

The electron density recovered using our direct-method algorithm is plotted over
balls representing Au atoms in a bulk-terminated structure in Fig. 5.3. The most
prominent feature of this result is the missing row along the $[\overline{1}10]$ (or x-) direction.

Comparing the positions of the electron density envelopes and those expected for a
bulk-terminated structure: some relaxation can be seen in the first layer, there are
also some hints of pairing in the second and fourth layers, and perhaps some buckling
Figure 5.2 (Color) yz projection of the autocorrelation map calculated with all the measured superstructure intensities. Coordinates are given in angstroms. Significant positive peaks can be found up to $z \approx 6\AA$. Taking the lowest layer of atoms in the surface region to be $\frac{1}{2}a_3 = 1.44\AA$ above the first bulk layer, we concluded that the vertical extent of the surface region is of the order $\sim 8\AA$.

in the third layer.

With the maxima in the electron density in Fig. 5.3 as the starting positions, conventional refinement of the atomic positions was carried out. In Fig. 5.4, the same electron density is plotted over balls representing Au atoms in our final model.

Results of our conventional refinement are summarized in Table 5.1. Structural parameters from our study agree very well with those reported earlier (Table 5.2) although none of the former studies had the capabilities to detect all the structural
Figure 5.3 (Color) yz projection of electron density (yellow/green) in near-surface region recovered by our direct-method algorithm. Red balls show positions of Au atoms in a bulk-terminated structure. Coordinates in the y and z directions are given in units of $a_2$ and $a_3$. 
Figure 5.4  (Color) Similar to Fig. 5.3, except red balls show positions of Au atoms in our final model.

parameters we are reporting here. LEED (low energy electron diffraction) is more sensitive to out-of-plane displacements (buckling) than in-plane displacements (pairing) whereas the previous SXRD study did not have access to the same range of out-of-plane momentum transfer vectors as in our study and thus was unable to detect any buckling.

Success with the known clean Au(110) (1 × 2) surface reconstruction gave us confidence that our direct-method algorithm is ready for solving unknown structures. The use of our direct-method algorithm to determine the unknown \( c(2 \times 2) \) and \( (\sqrt{3} \times \sqrt{3}) \ R54.7^{\circ} \) reconstructions of Sb/ Au(110) are described in the next two chapters.
Table 5.1 Our final model for Clean Au (110) (1 × 2) surface reconstruction. See Fig. 5.5 for labels of atoms. In a bulk-terminated structure, z separation between adjacent layers is $\frac{1}{2}a_3$ and neighboring atoms within the same layer have the same z and are separated in the y direction by $a_2$. Parameters specifying deviation from bulk-terminated structure are given in the left-hand columns: $\Delta d_{\alpha\beta}$ is for the z separation between layers $\alpha$ and $\beta$, and $b_\alpha$ and $p_\alpha$ respectively are for the z and y separations between adjacent atoms in layer $\alpha$. In other words, $\Delta d_{\alpha\beta}$ is a measure of the contraction (-) or expansion (+) of layer $\alpha$, and $b_\alpha$ and $p_\alpha$ are respectively measures of buckling and pairing in layer $\alpha$. In the right-hand columns, $B_\alpha$ is the Debye-Waller factor of layer $\alpha$. Reduced $\chi^2$ of this model is 2.00.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>$B_\alpha$</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta d_{12}$</td>
<td>$(z_1 - z_2) - \frac{1}{2}a_3$</td>
<td>$-0.28 \pm 0.03\text{Å}$</td>
<td>$B_1$</td>
<td>$2.10\text{Å}^2$</td>
</tr>
<tr>
<td>$p_2 = \frac{1}{2} [a_2 - (y_{2B} - y_{2A})]$</td>
<td>$0.05 \pm 0.01\text{Å}$</td>
<td>$B_2$</td>
<td>$1.49\text{Å}^2$</td>
<td></td>
</tr>
<tr>
<td>$\Delta d_{23} = (z_2 - z_3) - \frac{1}{2}a_3$</td>
<td>$0.01 \pm 0.01\text{Å}$</td>
<td>$B_3$</td>
<td>$0.74\text{Å}^2$</td>
<td></td>
</tr>
<tr>
<td>$b_3 = z_{3B} - z_{3A}$</td>
<td>$0.29 \pm 0.03\text{Å}$</td>
<td>$B_4$</td>
<td>$0.56\text{Å}^2$</td>
<td></td>
</tr>
<tr>
<td>$p_4 = \frac{1}{2} [a_2 - (y_{4B} - y_{4A})]$</td>
<td>$0.04 \pm 0.01\text{Å}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.5 Label assignment for atoms in our final model (Table 5.1).
Table 5.2 Comparison of experimental structural parameters for Au(110) (1 × 2) surface reconstruction. See Table 5.1 and Fig. 5.5 for definitions of structural parameters. The LEED (low energy electron diffraction), MEIS (medium energy ion scattering) and SXRD results were respectively obtained by Moritz and Wolf (1985), Copel and Gustafsson (1986) and Vlieg et al. (1990). As can be seen from this comparison, our results agree very well with models proposed by other researchers.
Chapter 6

Sb/ Au(110) \(c(2 \times 2)\)

6.1 Introduction

When a Au(110) substrate is covered with about half a monolayer of Sb, the resulting structure exhibits a \(c(2 \times 2)\) reconstruction. This chapter is an account of the determination of the surface structure of Sb/ Au(110) \(c(2 \times 2)\) by surface x-ray diffraction. In Sec. 6.2, the in-plane diffraction pattern is examined to determine the size and orientation of the real space surface unit cell. We will see that this pattern is consistent with a centered \((2 \times 2)\) (or \(c(2 \times 2)\)) surface superstructure. To determine the internal structure of the \(c(2 \times 2)\) surface unit cell, we first attempt, in Sec. 6.3, to deduce its projected structure by using the partial Patterson function calculated from the in-plane superstructure Bragg reflections. We will point out that this Patterson function contains no useful information other than confirming the \(c(2 \times 2)\) symmetry of the diffraction data, and cannot be used to distinguish between alternative models. Then, in Sec. 6.4, we apply our direct-method algorithm to the measured data, the result of which suggests a model in which every other surface substitutional site (or hollow site) is occupied by a Sb atom, with the remaining ones occupied by Au atoms, resulting in a checkerboard arrangement. Finally, in Sec. 6.5, conventional refinement method is used to obtain the final structure solution.
6.2 Surface unit cell from in-plane diffraction pattern

Fig. 6.1 is a schematic diagram of the observed diffraction pattern. Nonzero diffraction intensities were found along rods with in-plane Laue indices \( h = \frac{m}{2} \) and \( k = \frac{n}{2} \), where \( m \) and \( n \) are both integers, and \( h \) and \( k \) are either both integers (CTRs) or both nonintegers (SRs). The diffraction intensities were observed to have the same \( p2mm \) symmetry as the Au (110) bulk.

![Figure 6.1 Schematic diagram of our observed diffraction pattern. Filled and unfilled circles denote crystal-truncation-rod (CTR) and superstructure-rod (SR) reflections respectively.](image)

The surface reconstruction that is consistent with this diffraction pattern has a rhombus-shaped unit cell with sides parallel to the two diagonals of the Au(110) bulk unit cell and area twice that of the latter (Fig. 6.2). It is, however, more convenient to choose a surface unit cell with the size and orientation of a \((2 \times 2)\) array of bulk unit cells (Fig. 6.2). Reconstruction with such surface unit cell, in general, produces nonzero diffraction intensities for all reflections with in-plane Laue indices \( h = \frac{m}{2} \) and \( k = \frac{n}{2} \) where \( m \) and \( n \) are both integers. CTR reflections have integer values for both \( h \) and \( k \); whereas SR reflections have noninteger values for either or both of the in-
plane Laue indices. For this general \((2 \times 2)\) diffraction pattern to reduce to the one observed experimentally, our \((2 \times 2)\) surface unit cell must be centered, i.e., for each inequivalent atom present in our \((2 \times 2)\) surface unit cell, an identical atom must be present exactly “one bulk unit cell diagonal vector” away (Fig. 6.3).

![Figure 6.2 Real space unit cells. The rectangle at the top left corner with dimensions \(a \times \sqrt{2}a\) represents a bulk unit cell. The rhombus with sides \(\sqrt{3}a\) parallel to the two diagonals of the bulk unit cell is one choice for the surface unit cell, area of which is twice that of a bulk unit cell. A more convenient choice is the \((2 \times 2)\) surface unit cell which has the size and orientation of a \((2 \times 2)\) array of bulk unit cells.](image)

With such atomic arrangement, the surface structure factor of reflection \((hkl)\) takes the form:

\[
S_{(hkl)} = \sum_j f_j \left\{ e^{2\pi i(hx_j + ky_j + lz_j)} + e^{2\pi i[(hx_j + 1) + ky_j + (lz_j + 1)]} \right\},
\]

\[
= \left[ 1 + e^{2\pi i(h+k)} \right] \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}, \tag{6.1}
\]

where the sum is over all inequivalent atoms \(j\), with form factors \(f_j\), within a \((2 \times 2)\) surface unit cell, and coordinates \((x_j, y_j, z_j)\) are expressed as fractions of the dimensions of a bulk unit cell. Thus intensity of reflection \((hkl)\) is nonzero only
Figure 6.3  (a) A bulk unit cell with its two diagonal vectors ($\vec{a}_1 \pm \vec{a}_2$). (b) In a $c(2 \times 2)$ unit cell ($c =$ centered,) real space features come in pairs, with the members of each pair separated by exactly “one bulk unit cell diagonal vector” (i.e. $\vec{a}_1 \pm \vec{a}_2$).

when

$$(h, k) = (m, n) \text{ or } \left(m + \frac{1}{2}, n + \frac{1}{2}\right),$$

(6.2)

where $m$ and $n$ are both integers.

### 6.3 Unit-cell contents from in-plane superstructure spot Patterson function

Using superstructure reflections with $l \approx 0$, the autocorrelation function for the present data is plotted in Fig. 6.4. Other than the trivial origin peak, strong peaks are also found at $2\vec{a}_1$, $2\vec{a}_2$, $(\vec{a}_1 + \vec{a}_2)$ and $2(\vec{a}_1 + \vec{a}_2)$. However, these peaks are merely the periodic repetition of the origin peak, reflecting the $c(2 \times 2)$ symmetry of the
diffraction pattern, and convey no new information. Several much weaker peaks can also be seen in Fig. 6.4 but these are probably due to noise or the fact that data for precisely \( l = 0 \) is not measurable.

Figure 6.4 (Color) Autocorrelation function for the present data, calculated using only in-plane superstructure reflections, showing interatomic vectors in a \((2 \times 2)\) unit cell. Warm colors correspond to high values. The strong peaks at \((0, 2), (1, 1), (2, 0)\) and \((2, 2)\) are just periodic repetition of the origin peak, reflecting the \( c(2 \times 2) \) symmetry of the diffraction data. This Patterson map thus conveys no useful information other than confirming the \( c(2 \times 2) \) symmetry of the diffraction data.

Knowing that each \((2 \times 2)\) surface unit cell contains two Sb adatoms \( (\theta_{\text{Sb}} \approx \frac{1}{2}) \), we proceed to refine by conventional means the four most “obvious” trial models. In these models, Sb adatoms are held over the hollow, atop, long bridge or short bridge sites (Fig. 6.5) of the last Au layer (taken to be unrelaxed.) All the atoms in the models are assigned the Debye-Waller factor of Au at RT and only the vertical positions of the Sb adatoms and the outermost Au layer are allowed to vary to minimize the reduced \( \chi^2 \). Results are summarized in Table 6.1. The Sb-Au bondlength(s) for each model is
given to facilitate comparison between the different models and the compound AuSb$_2$ for which the Sb-Au bondlength is 2.763 Å (Furuseth et al. (1965)). As expected, occupation of hollow sites is preferred. However, all $\chi^2$ values are significantly higher than would be expected for a correct structural model.

![Diagram of high symmetry models containing one inequivalent Sb adatom in the $c(2 \times 2)$ surface unit cell. In the schematics, Au atoms in the outermost Au layer are at the corners of the bulk unit cells. Fractional $(x, y)$ coordinates of the Sb adatoms are listed in column 2 of Table 6.1.]

Since none of these “obvious” models seem particularly promising, we turn to our direct-method algorithm.
Table 6.1 Conventional fitting results for the four high symmetry models: hollow, atop, long bridge and short bridge. Column 2 lists the fractional $(x, y)$ coordinates, relative to a Au atom in the last Au layer, over which the Sb adatoms were held. The Sb adatoms were initially placed at half the height of a bulk unit cell above the last Au layer, which was taken to be unrelaxed. Changes in $z$ positions of the Sb atoms and the last Au layer that minimized the reduced $\chi^2$ are listed in columns 3 and 4. The resultant Sb-Au bondlengths are listed in column 5. All atoms in the models were assigned Debye-Waller factor of bulk Au at RT.

### 6.4 Application of our direct-method algorithm

The electron density recovered using our direct-method algorithm (Fig. 2.8 and Eqs. (2.63) to (2.67)) is shown in Figs. 6.6 and 6.7. These plots clearly show that every surface substitutional site (or hollow site) is occupied (instead of every other one.) It is also obvious from these figures that the charge density in half the sites is greater than in the other half. This suggests a model where every other hollow site is occupied by a Sb adatom, with the rest occupied by Au adatoms, resulting in a checkerboard arrangement (Fig. 6.8).
Figure 6.6 (Color) Electron density in near-surface region recovered by our direct-method algorithm. xy, yz and xz projections are shown. Coordinates in the x, y and z directions are respectively given in units of $a_1$, $a_2$ and $a_3$. Note that, for these plots, a Au atom in the second-last Au layer (not the outermost one) is placed at the origin.
Figure 6.7 (Color) Electron density in near-surface region recovered by our direct-method algorithm. Warm colors correspond to high values. Two-dimensional cuts through xy planes located at $z/a_3 = 1.125$ (top) and $z/a_3 = 0.625$ (bottom) are shown, showing atoms in the surface layer and the outermost Au layer respectively. Note that, for these plots, a Au atom in the second-last Au layer (not the outermost one) is placed at the origin.
Figure 6.8 Atomic model suggested by the results of our direct-method algorithm: every other surface substitutional site (or hollow site) is occupied by a Sb atom (denoted by circles,) with the remaining ones occupied by Au atoms (denoted by triangles,) resulting in a checkerboard arrangement. In the schematic, Au atoms in the outermost Au layer are at the corners of the bulk unit cells.

This new model is consistent with our observed Patterson map which is calculated using SR reflections with $l \approx 0$ (Eq. (1.19)):

$$P(\vec{r}) = \frac{1}{N} \sum_{\vec{q} \in \{\vec{q}_{SR}, l \approx 0\}} |S_{\vec{q}}|^2 \cos(2\pi \vec{q} \cdot \vec{r}).$$

(6.3)

For fractional-order reflections, the in-plane Laue indices are $(h, k) = (m + \frac{1}{2}, n + \frac{1}{2})$, where $m$ and $n$ are integers. Thus the cosine term in Eq. (6.3) takes the form

$$\cos \left\{ 2\pi \left[ \left( m + \frac{1}{2} \right) x + \left( n + \frac{1}{2} \right) y \right] \right\},$$

which for integers $x$ and $y$ (corresponding to bulk lattice vectors) reduces to $\cos[\pi(x + y)]$ and is positive only if $x + y$ is a multiple of two, e.g. $(x, y) = (0, 0), (0, 2), (1, 1), (2, 0), \text{ or } (2, 2)$ etc. The Sb-Au interatomic vectors, e.g. $(x, y) = (0, 1), (1, 0)$ etc, therefore, do not show up as positive peaks in our Patterson map.
6.5 Conventional structure refinement

Preliminary conventional fitting of the model suggested by our direct method (Fig. 6.8) was first performed in which the lateral positions of all the adatoms were held fixed and their Debye-Waller factors were taken as the same as that of bulk Au at RT. Starting with all adatoms at half the height of a bulk unit cell above the outermost Au layer and directly over the hollow site, the vertical positions of the adatoms and the outermost Au layer were allowed to vary. The best-fit model yielded a reduced $\chi^2$ of 2.52, much lower than that of the previous models. Details of the fit are summarized in Table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta z$ (Å)</th>
<th>bondlength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb $(\frac{x}{a_1}, \frac{y}{a_2}) = (\frac{1}{2}, \frac{1}{2}), (\frac{3}{2}, \frac{3}{2})$</td>
<td>-0.08</td>
<td>2.76</td>
</tr>
<tr>
<td>Au $(\frac{x}{a_1}, \frac{y}{a_2}) = (\frac{1}{2}, \frac{3}{2}), (\frac{3}{2}, \frac{1}{2})$</td>
<td>0.08</td>
<td>2.83</td>
</tr>
<tr>
<td>Au layer</td>
<td>0.19</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 6.2 Conventional fitting results for the model suggested by our direct-method algorithm (Fig. 6.8). Surface atoms were initially placed at half the height of a bulk unit cell above the last Au layer, directly over the hollow sites. Changes in $z$ positions of the surface atoms and relaxation of the last Au layer that minimized the reduced $\chi^2$ are listed. The distances between the adatoms and the closest Au atom (bondlengths) are also listed. All atoms in the model were assigned Debye-Waller factor of bulk Au at RT. Reduced $\chi^2$ of this model (with restricted free parameters) is 2.52.

An even lower reduced $\chi^2$ of 1.45 is obtained if the adatoms and the Au atoms
in the outermost bulk layer are allowed to have Debye-Waller factors different from that of bulk Au at RT. The values of Debye-Waller factors for the adatoms in this model (Table 6.3) seem somewhat high.\(^1\) Allowing for partial occupancies\(^2\) reduces these Debye-Waller factors to be within reasonable range. The final reduced $\chi^2$ value of 0.90 indicates that our final model (Table 6.4) is in very good agreement with the data.

$$\Delta z (\text{\AA}) \quad B (\text{\AA}^2)$$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta z$ (\AA)</th>
<th>$B$ (\text{\AA}$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb (\frac{x}{a_1}, \frac{y}{a_2}) = (\frac{1}{2}, \frac{1}{2}), (\frac{3}{2}, \frac{3}{2})</td>
<td>-0.17 ± 0.01</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>Au (\frac{x}{a_1}, \frac{y}{a_2}) = (\frac{1}{2}, \frac{3}{2}), (\frac{3}{2}, \frac{1}{2})</td>
<td>0.00 ± 0.01</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>Au layer</td>
<td>0.15 ± 0.00</td>
<td>1.1 ± 0.1</td>
</tr>
</tbody>
</table>

Table 6.3 Conventional fitting results for the model suggested by our direct-method algorithm (Fig. 6.8). Surface atoms were initially placed at half the height of a bulk unit cell above the last Au layer, directly over the hollow sites. Changes in $z$ positions and Debye-Waller factors of the adatoms and the atoms in the last Au layer that minimized the reduced $\chi^2$ are listed. Reduced $\chi^2$ of this model is 1.45.

\(^1\)Debye-Waller factor $B$ and mean-square vibrational amplitude $\langle (\Delta r)^2 \rangle$ of an atom are related by $B = 8\pi^2 \langle (\Delta r)^2 \rangle$. This is derived in Sec. A.2. When $B \approx 3\text{\AA}^2$, root-mean-square vibrational amplitude $\sqrt{\langle (\Delta r)^2 \rangle} \approx 0.19\text{\AA}$.

\(^2\)Partial occupancy:

Sb/ Au (110) surface exhibits $c(2 \times 2)$ reconstruction for a range of Sb coverage. This range was established in UWM where the technique of LEED (low energy electron diffraction) was used to monitor the in-plane diffraction pattern as more and more Sb was deposited onto a Au (110) substrate. The technique of XPS (x-ray photoelectron spectroscopy) (Sec. 4.1) was used to determine the Sb coverage.

The SXRD endstation at NSLS (National Synchrotron Light Source at Brookhaven National Laboratory), where the sample was prepared and the diffraction data were collected, lacks XPS capabilities, the Sb coverage of our sample was therefore not measured during the SXRD experiment and could have been lower than $\theta_{\text{Sb}} = \frac{1}{2}$. 
Table 6.4 Conventional fitting results for the model suggested by our direct-method algorithm (Fig. 6.8). Comments given in Table 6.3’s caption apply here, except occupancies of the adatoms are also allowed to vary. Reduced $\chi^2$ of this model is 0.90.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta z (\text{Å})$</th>
<th>$B (\text{Å}^2)$</th>
<th>occ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb ($\frac{x}{a_1}, \frac{y}{a_2}$) = ($\frac{1}{2}, \frac{1}{2}$), ($\frac{3}{2}, \frac{3}{2}$)</td>
<td>$-0.21 \pm 0.01$</td>
<td>$1.3 \pm 0.1$</td>
<td>$0.77 \pm 0.01$</td>
</tr>
<tr>
<td>Au ($\frac{x}{a_1}, \frac{y}{a_2}$) = ($\frac{1}{2}, \frac{3}{2}$), ($\frac{3}{2}, \frac{1}{2}$)</td>
<td>$0.00 \pm 0.01$</td>
<td>$1.5 \pm 0.1$</td>
<td>$0.71 \pm 0.01$</td>
</tr>
<tr>
<td>Au layer</td>
<td>$0.13 \pm 0.00$</td>
<td>$1.5 \pm 0.1$</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Chapter 7

\[ \text{Sb} / \text{Au(110)} \ (\sqrt{3} \times \sqrt{3}) \ R^{54.7^\circ} \]

7.1 Introduction

When a Au(110) substrate is covered with about two thirds of a monolayer of Sb, the resulting structure exhibits a \((\sqrt{3} \times \sqrt{3})\) reconstruction. This chapter is an account of the determination of the surface structure of \((\sqrt{3} \times \sqrt{3})\) Sb/Au(110) by surface x-ray diffraction. First we will discuss in Sec. 7.2 what may be deduced about the structure from an examination of the in-plane diffraction pattern. We will see that this pattern can arise from the superposition of diffraction patterns from four symmetrically-related domains of \((\sqrt{3} \times \sqrt{3})\) surface superstructures. The next step is the determination of the internal structure of the \((\sqrt{3} \times \sqrt{3})\) surface unit cells. We begin in Sec. 7.3 by attempting to deduce the projected structure of the surface unit cell from the partial Patterson function calculated from the in-plane superstructure Bragg reflections. We will point out that this Patterson function does not contain enough information to distinguish between alternative models. Then in Sec. 7.4 we apply our direct-method algorithm to the measured data. This immediately suggests a model in which two Sb adatom diagonal rows alternate with a row of Au adatoms, all adatoms in hollow sites on the surface. In Sec. 7.5, we provide an account of an application of a conventional refinement method for the final structure solution. We conclude this chapter with some interesting observations about the fractional
Patterson function in Sec. 7.6.

### 7.2 Surface unit cell from in-plane diffraction pattern

Nonzero diffraction intensities were found along rods with in-plane Laue indices $h = \frac{m}{3}$ and $k = \frac{n}{3}$, where $m$ and $n$ are both integers, and $h$ and $k$ are either both integers (CTRs) or both nonintegers (SRs). Fig. 7.1 is a schematic diagram of the observed diffraction pattern. The diffraction intensities were observed to have the same $p2mm$ symmetry as the Au (110) bulk.

![Schematic diagram of observed diffraction pattern](image)

Figure 7.1 Schematic diagram of our observed diffraction pattern. Filled and unfilled circles denote crystal-truncation-rod (CTR) and superstructure-rod (SR) reflections respectively. Unfilled circles with thick and thin outlines represent SR reflections arising from surface domains with different orientations. The two types of surface domains are referred to as type 1 (thick outline) and type 2 (thin outline) in the main text.

This diffraction pattern is consistent with a surface reconstruction in which the surface unit cells are similar rectangles to that of the bulk unit cell, but $\sqrt{3}$ times
larger in linear dimensions, and rotated by 54.7° relative to the latter. Half of
the superstructure reflections (Fig. 7.1, unfilled circles with thick outline) can be
accounted for by having domains (type 1) in which the surface lattice vectors are
rotated 54.7° clockwise from the bulk lattice vectors (Fig. 7.2), the other half (Fig. 7.1,
unfilled circles with thin outline,) requires domains (type 2) in which the rotation is
in the counterclockwise sense.

![Figure 7.2 Real space unit cells. The rectangle at the top left corner with dimensions $a \times \sqrt{2}a$ represents a bulk unit cell. The rotated rectangle with dimensions $\sqrt{3}a \times \sqrt{6}a$ is a type-1 $(\sqrt{3} \times \sqrt{3})$ surface unit cell. Its sides make angles 54.7° with those of the bulk unit cell. Finally, the $(3 \times 3)$ surface unit cell has the size and orientation of a $(3 \times 3)$ array of bulk unit cells.](image)

Features in such surface unit cells line up to form rows parallel to one of the two
diagonals of the bulk unit cells (Fig. 7.3).

An alternative way to describe the reconstruction is to have rectangular surface
unit cells with the size and orientation of a $(3 \times 3)$ array of bulk unit cells (Fig. 7.2). Reconstruction with such surface unit cells, in general, produces nonzero diffraction intensities for all reflections with in-plane Laue indices $h = \frac{m}{3}$ and $k = \frac{n}{3}$ where $m$ and $n$ are both integers. CTR reflections have integer values for both $h$ and $k$; whereas SR reflections have noninteger values for either or both of the in-plane Laue indices. For this general $(3 \times 3)$ diffraction pattern to reduce to the one observed experimentally, certain extinction conditions must be met.

These conditions arise for the following reasons: as pointed out before, the contents of the $(3 \times 3)$ surface unit cell in real space must be such that features form rows parallel to one of the two diagonals of the bulk unit cells, resulting in the same
arrangement as in the previous \((\sqrt{3} \times \sqrt{3})\) description (Fig. 7.2). If only type-1 surface unit cells are present (Fig. 7.3), the surface structure factor of reflection \((hkl)\) takes the form:

\[
S_{(hkl)} = \sum_j f_j \left\{ e^{2\pi i(hx_j+ky_j+ lz_j)} + e^{2\pi i[h(x_j+1)+k(y_j-1)+lz_j]} + e^{2\pi i[h(x_j+2)+k(y_j-2)+lz_j]} \right\},
\]

\[
= \left[ 1 + e^{2\pi i(h-k)} + e^{2\pi i(2h-2k)} \right] \sum_j f_j e^{2\pi i(hx_j+ky_j+lz_j)},
\]

(7.1)

where the sum is over all inequivalent atoms \(j\), with form factors \(f_j\), within a \((3 \times 3)\) surface unit cell, and coordinates \((x_j,y_j,z_j)\) are expressed as fractions of the dimensions of a bulk unit cell. Thus intensity of reflection \((hkl)\) is nonzero only when

\[
(h,k) = (m,n) \text{ or } \left( m \pm \frac{1}{3}, n \pm \frac{1}{3} \right),
\]

(7.2)

where \(m\) and \(n\) are both integers. Similarly, if only type-2 surface unit cells are present, intensities of only reflections \((hkl)\) with

\[
(h,k) = (m,n) \text{ or } \left( m \pm \frac{1}{3}, n \mp \frac{1}{3} \right),
\]

(7.3)

where \(m\) and \(n\) are both integers, will be nonzero. Both types of surface unit cells must be present to give the observed diffraction pattern.

This alternative \((3 \times 3)\) description provides an insight that would not have been as obvious with the previous \((\sqrt{3} \times \sqrt{3})\) description, namely that four domains are required, in general, to ensure \(p2mm\) symmetry is preserved. Two examples are given in Fig. 7.4 to illustrate this point, which is important for the proper implementation of both our direct-method algorithm and conventional least-squares fitting.
Figure 7.4 Examples to illustrate the need for four domains. In each case, crosses, squares and circles represent atoms of different species at different heights. Domains 1 and 4 are of type 1 and domains 2 and 3 are of type 2. Domains 1 and 2 are related by a vertical mirror plane, so are domains 3 and 4. Similarly, domains 1 and 3 are related by a horizontal mirror plane and so are domains 2 and 4. These four domains are different in general and therefore all four are required to preserve $p2mm$ symmetry. If domains 2 and 3 are identical, in which case domains 1 and 4 will also be identical, then only two domains are needed. (a) Atoms in one of the four high-symmetry (atop, hollow, long bridge or short bridge) sites, unless atoms represented by squares and circles are of the same species and are at the same height, the four domains are different. (b) Atoms in general locations.

For a multi-domain system where domain sizes are greater than the coherence length of the x-ray probe, measured intensities \( \{ I \} \) are incoherent averages of contributions from the various domains:

\[
I = \frac{1}{N_{\text{domain}}} \sum_{j=1}^{N_{\text{domain}}} |B_j + S_j|^2. \tag{7.4}
\]

Here \( N_{\text{domain}} \) is the number of domains present, and \( B_j \) and \( S_j \) are respectively contributions to structure factors from the bulk and the surface layer of domain \( j \). In particular, for the present case where in general there are four domains, we have

\[
I = \frac{1}{4}(|B_1 + S_1|^2 + |B_2 + S_2|^2 + |B_3 + S_3|^2 + |B_4 + S_4|^2). \tag{7.5}
\]
The four domains have the same underlying bulk and therefore the same bulk contributions to structure factors: \( B_1 = B_2 = B_3 = B_4 = B \). The four surface contributions form two 2D inversion pairs (i.e. \( x \rightarrow -x, \ y \rightarrow -y \)), thus for in-plane reflections \((l = 0)\), using the domain notations introduced in Fig. 7.4, we have \( S_4 = S_1^* \) for the two type-1 domains and \( S_3 = S_2^* \) for the two type-2 domains. Thus, Eq. (7.5) becomes

\[
I_{(h0)} = \frac{1}{4}(|B + S_1|^2 + |B + S_2|^2 + |B + S_2^*|^2 + |B + S_1^*|^2).
\tag{7.6}
\]

For in-plane SR reflections arising from type-1 domains, Eq. (7.6) reduces to

\[
I_{(h0)} = \frac{1}{4}(|S_1|^2 + |S_1^*|^2) = \frac{1}{2}|S_1|^2 = \frac{1}{2}|S_4|^2.
\tag{7.7}
\]

The two type-1 domains therefore contribute equally to these intensities, and autocorrelation function calculated using these intensities will give a map of interatomic vectors between x-ray scatterers in the surface region of both type-1 domains.

### 7.3 Unit-cell contents from in-plane superstructure spot Patterson function

It is important to note that all experimentally available superstructure reflections are used in the calculation of autocorrelation function for either type-1 or type-2 domains, the reflections are just labeled differently in the two cases. This is illustrated in Fig. 7.5.
Figure 7.5 Schematic diagram showing how data are symmetrized. Due to $p2mm$ symmetry, only data for positive $h$ and $k$ need to be collected. In the example here, four inequivalent superstructure reflections are measured (denoted by different unfilled geometric shapes: cross, diamond, circle and square.) Intensities of reflections in the other quadrants are obtained using symmetry. The four reflections denoted by the unfilled squares, for instance, have the same intensities. To calculate autocorrelation function for, say, a type-1 domain, reflections denoted by unfilled shapes with thick outline are used. As can be seen in the schematic, all measured inequivalent superstructure reflections (i.e. cross, diamond, circle and square) are used.

Using superstructure reflections with $l \approx 0$ that arise from type-1 domains, autocorrelation function for the present data is plotted in Fig. 7.6. Other than the trivial origin peak, strong peaks are also found at $\vec{a}_1 + 2\vec{a}_2$ and $2\vec{a}_1 + \vec{a}_2$. However, these peaks merely reflect the $(\sqrt{3} \times \sqrt{3})$ symmetry of the diffraction pattern and do not provide any new insights into the atomic arrangement of the surface layer. If we take the weaker peaks to be due to noise or the fact that data for precisely $l = 0$ are not measurable, this Patterson map seems, at first sight, to be in contradiction with our Sb adatom coverage. A coverage of $\theta_{Sb} \approx \frac{2}{3}$ would correspond to six Sb adatoms, or two parallel rows, per $(3 \times 3)$ surface unit cell. The two peaks at $\vec{a}_1 + 2\vec{a}_2$ and $2\vec{a}_1 + \vec{a}_2$ correspond to the interatomic vectors within each row, but the interatomic
vectors *between* the two rows seem to be missing.

The observed Patterson map is in fact consistent with two rows of Sb adatoms on each \((3 \times 3)\) surface unit cell, separated laterally by exactly a 2D bulk lattice vector. We will now show that in this case the interatomic vectors between Sb atoms on different rows, e.g. \(\vec{a}_1\), or \(\vec{a}_2\) etc, do not show up as positive peaks in a fractional Patterson map.
Recall that fractional Patterson function is given by (Eq. (1.19)):

\[
P(\vec{r}) = \frac{1}{N} \sum_{\vec{q} \in \{\vec{q}_{SR}, l \approx 0\}} |S_{\vec{q}}|^2 \cos(2\pi \vec{q} \cdot \vec{r}).
\]  

(7.8)

For a type-1 domain, the cosine term in Eq. (7.8) takes the form:

\[
\cos \left\{2\pi \left[ \left( m \pm \frac{1}{3} \right) x + \left( n \pm \frac{1}{3} \right) y \right] \right\},
\]  

(7.9)

which for integers \(x\) and \(y\) (corresponding to 2D bulk lattice vectors) reduces to \(\cos \left[\frac{2\pi}{3}(x + y)\right]\) and is positive only if \(x + y\) is a multiple of three, e.g. \((x, y) = (0, 0), (1, 2)\) or \((2, 1)\) etc. These are the lattice vectors of a type-1 \((\sqrt{3} \times \sqrt{3})\) surface unit cell and are the only interatomic vectors observed in Fig. 7.6. The interatomic vectors between Sb atoms on different rows, e.g. \((x, y) = (1, 0), (0, 1)\) etc, therefore, do not show up as positive peaks in our Patterson map.

Knowing that each \((3 \times 3)\) surface unit cell contains six Sb adatoms \(\left( \theta_{Sb} \approx \frac{2}{3} \right)\) forming two parallel rows, and that the two rows must be separated laterally by a 2D bulk lattice vector (Patterson map,) we proceed to refine by conventional means the four most “obvious” trial models. In these models, Sb adatoms are placed at half the height of a bulk unit cell (i.e. \(\frac{1}{2}a_3\)) above the last Au layer (taken to be unrelaxed,) over the hollow, atop, long bridge or short bridge sites (Fig. 7.7). All the atoms in the models are assigned the Debye-Waller factor of Au at RT and only the vertical positions of the Sb adatoms and the first Au layer are allowed to vary to minimize the reduced \(\chi^2\). Results are summarized in Table 7.1. As expected, occupation of hollow sites is preferred. However, all \(\chi^2\) values are significantly higher than would be expected for a correct structural model.
Since none of these “obvious” models seem particularly promising, we turn to our direct-method algorithm.

### 7.4 Application of our direct-method algorithm

The basic iteration scheme of our direct-method algorithm (Fig. 2.8 and Eqs. (2.63) to (2.67)) applies only to single-domain systems. Take Eq. (2.67) for instance, \( \{ B \} \)
Table 7.1  Conventional fitting results for the four high symmetry models: hollow, atop, long bridge and short bridge in a type-1 domain configuration (Fig. 7.7). Columns 2 and 3 list the fractional \((x, y)\) coordinates, relative to a Au atom in the last Au layer, over which the Sb adatoms were held. The Sb adatoms were initially placed at half the height of a bulk unit cell above the last Au layer, which was taken to be unrelaxed. Changes in \(z\) positions (\(\text{Å}\)) of the Sb adatoms and the last Au layer that minimized the reduced \(\chi^2\) are listed. All atoms in the models were assigned Debye-Waller factor of bulk Au at RT.

can only be subtracted from \(\{F\}\) if they are both single-domain structure factors.

In the presence of multiple domains however, the measured quantity \(\{|F_{\text{obs}}|\}\) is an average over domains. For multi-domain systems, Eq. (2.66) must be generalized to serve as the link between single-domain and domain-averaged quantities.

For a multi-domain system, where domain sizes are larger than the coherence length of the x-ray probe, measured intensities are incoherent averages of contributions from all the domains (Eq. (7.4)). The intensity contribution from one domain is therefore:

\[
|F_i|^2 = |B_1 + S_1|^2 = N_{\text{domain}}I - \sum_{j=2}^{N_{\text{domain}}} |B_j + S_j|^2.
\]  
(7.10)
Thus, Eq. (2.66) generalizes to:

\[
\{ F^{(n+1)} \} = \left\{ \sqrt{N_{\text{domain}} |F_{\text{obs}}|^2 - \sum_{j=2}^{N_{\text{domain}}} |B_j + S_j^{(n+1)}|^2} \exp(i\phi_{\text{calc}}^{(n+1)}) \right\}.
\] (7.11)

In particular, in the case of four domains with the same underlying bulk structure,

\[
|F_1|^2 = 4I - \sum_{j=2}^{4} |B_j + S_j|^2,
\] (7.12)

and therefore

\[
\{ F^{(n+1)} \} = \left\{ \sqrt{4|F_{\text{obs}}|^2 - \sum_{j=2}^{4} |B_j + S_j^{(n+1)}|^2} \exp(i\phi_{\text{calc}}^{(n+1)}) \right\}.
\] (7.13)

The electron density (Fig. 7.8) recovered using our direct-method algorithm clearly shows that there are three rows of atoms, close to but not directly above the hollow sites. Also, the electron density of the features in one of the three rows is clearly greater than in the other two. This suggests a model with two rows of Sb and one row of Au close to the hollow sites of a \((3 \times 3)\) surface unit cell (Fig. 7.9). This new model is consistent with our observed Patterson map since, as argued before, any interatomic spacing that corresponds to a 2D bulk lattice vector but not to a \((\sqrt{3} \times \sqrt{3})\) surface lattice vector will not show up in the fractional Patterson map.

### 7.5 Conventional structure refinement

As suggested in the Introduction chapter, the aim of a direct method is to suggest the broad outline of the correct model. Accurate values of structural parameters are
Figure 7.8 (Color) Electron density in near-surface region recovered by our direct-method algorithm. xy-, yz- and xz- projections are shown. Coordinates in the x-, y- and z-directions are respectively given in units of $a_1$, $a_2$ and $a_3$. 
still best found by conventional refinement methods. Accordingly, we attempted to refine these parameters in the usual way, starting with a model of adatoms at half the height of a bulk unit cell above the outermost Au layer and directly over the hollow sites (Fig. 7.9). In addition to the vertical positions of the adatoms and the outermost Au layer, the lateral positions of the adatoms were allowed to vary in all directions, subject to symmetry restrictions. The best-fit model yielded a reduced $\chi^2$ value of 2.35, much lower than that of the previous models. Details of the fit are summarized in Table 7.2.

An even lower reduced $\chi^2$ of 1.74 is obtained if the adatoms and the Au atoms in the outermost bulk layer are allowed to have Debye-Waller factors different from that of bulk Au atoms at RT. The elevated values of Debye-Waller factors for the two Sb adatoms in this model (Table 7.3) may be somewhat troubling. Allowing for partial occupancies reduces these Debye-Waller factors to be within reasonable range,
Table 7.2 Conventional fitting results for the model suggested by our direct-method algorithm (Fig. 7.9). Surface atoms were initially placed at half the height of a bulk unit cell above the last Au layer, directly over the hollow sites. Changes in positions of the surface atoms and relaxation of the last Au layer that minimized the reduced $\chi^2$ are listed. All atoms in the model were assigned Debye-Waller factor of bulk Au at RT. Reduced $\chi^2$ of this model (with restricted free parameters) is 2.35.

but with high error bars. It is worth noting that we would not expect to observe $(\sqrt{3} \times \sqrt{3}) \ R54.7^\circ$ reconstruction at the Sb coverage implied by the occupancies of the Sb adatoms in our final model (Table 7.4). More work needs to be done to ascertain the origin of this discrepancy.
Table 7.3 Conventional fitting results for the model suggested by our direct-method algorithm (Fig. 7.9). Comments given in Table 7.2’s caption apply here, except Debye-Waller factors of the adatoms and Au atoms in the last layer are also allowed to vary. Reduced $\chi^2$ for this model is 1.74.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta x$ (Å)</th>
<th>$\Delta y$ (Å)</th>
<th>$\Delta z$ (Å)</th>
<th>$B$ (Å$^2$)</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_1$</td>
<td>$-0.16 \pm 0.01$</td>
<td>$-0.19 \pm 0.01$</td>
<td>$-0.29 \pm 0.02$</td>
<td>$4.2 \pm 0.2$</td>
<td></td>
</tr>
<tr>
<td>Sb$_2$</td>
<td>$0.05 \pm 0.01$</td>
<td>$-0.01 \pm 0.01$</td>
<td>$0.61 \pm 0.02$</td>
<td>$10 \pm 1$</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>$-0.03 \pm 0.01$</td>
<td>$0.03 \pm 0.01$</td>
<td>$-0.05 \pm 0.01$</td>
<td>$1.3 \pm 0.0$</td>
<td></td>
</tr>
<tr>
<td>Au layer</td>
<td>N/A</td>
<td>N/A</td>
<td>$0.11 \pm 0.00$</td>
<td>$1.1 \pm 0.0$</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.4 Conventional fitting results for the model suggested by our direct-method algorithm (Fig. 7.9). Comments given in Table 7.2’s caption apply here, except Debye-Waller factors of the adatoms and Au atoms in the last layer, as well as the occupancies of the adatoms are also allowed to vary. Reduced $\chi^2$ for this model is 1.51.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta x$ (Å)</th>
<th>$\Delta y$ (Å)</th>
<th>$\Delta z$ (Å)</th>
<th>$B$ (Å$^2$)</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_1$</td>
<td>$-0.09 \pm 0.01$</td>
<td>$-0.20 \pm 0.01$</td>
<td>$-0.23 \pm 0.02$</td>
<td>$1.1 \pm 0.6$</td>
<td>$0.69 \pm 0.05$</td>
</tr>
<tr>
<td>Sb$_2$</td>
<td>$0.10 \pm 0.01$</td>
<td>$0.03 \pm 0.01$</td>
<td>$0.47 \pm 0.01$</td>
<td>$0.67 \pm 0.51$</td>
<td>$0.61 \pm 0.02$</td>
</tr>
<tr>
<td>Au</td>
<td>$0.06 \pm 0.00$</td>
<td>$0.04 \pm 0.01$</td>
<td>$-0.12 \pm 0.01$</td>
<td>$1.4 \pm 0.1$</td>
<td>$0.96 \pm 0.01$</td>
</tr>
<tr>
<td>Au layer</td>
<td>N/A</td>
<td>N/A</td>
<td>$0.10 \pm 0.00$</td>
<td>$1.0 \pm 0.0$</td>
<td>N/A</td>
</tr>
</tbody>
</table>
7.6 Some Patterson Function “Musings”

Using Eq. (7.8) for fractional Patterson function, we have argued that the observed Patterson map is consistent with the surface layer having (i) one row of Sb adatoms, (ii) two rows of Sb adatoms separated laterally by a 2D bulk lattice vector, or (iii) two Sb adatom rows alternate with one row of Au adatoms, all separated by 2D bulk lattice vectors. The argument was made by pointing out that, for systems with \((\sqrt{3} \times \sqrt{3})\) symmetry, fractional Patterson functions cannot have positive peak for any interatomic vector that corresponds to a 2D bulk lattice vector unless that vector also corresponds to a 2D surface lattice vector.

We will now show that fractional Patterson maps for the first two systems described above are in fact identical. We will look at Patterson maps of systems with two or three inequivalent atoms separated by 2D bulk lattice vectors and some general remarks will be made.

With only one inequivalent atom, contribution of a type-1 \((3 \times 3)\) surface unit cell to the structure factor of reflection \((hk0)\) is (Eq. (7.1)):

\[
S_{(hk0)} = \left[1 + e^{2\pi i(h-k)} + e^{2\pi i(2h-2k)}\right]f_1 e^{2\pi i(hx_1+ky_1)}.
\]  

(7.14)

Adding a second inequivalent atom \(\vec{a}_1\) from the first gives:

\[
S_{(hk0)} = \left[1 + e^{2\pi i(h-k)} + e^{2\pi i(2h-2k)}\right]\left\{f_1 e^{2\pi i(hx_1+ky_1)} + f_2 e^{2\pi i[h(x_1+1)+ky_1]}\right\},
\]

\[
= \left[1 + e^{2\pi i(h-k)} + e^{2\pi i(2h-2k)}\right]f_1 e^{2\pi i(hx_1+ky_1)} \left[1 + \frac{f_2}{f_1} e^{2\pi ih}\right].
\]  

(7.15)

Noting the values \(h\) can take, we conclude that introduction of the second inequivalent
atom (or row of atoms) modifies $S_{(hk0)}$ by the complex factor:

$$
\Phi_{\pm} = \left[ 1 + \frac{f_2}{f_1} e^{\pm 2\pi i \frac{3}{2}} \right] = \left[ 1 - \frac{f_2}{2f_1} \pm i\frac{\sqrt{3}f_2}{2f_1} \right],
$$

(7.16)

and $I_{(hk0)} \left( = |S_{(hk0)}|^2 \right)$ by the real factor:

$$
|\Phi_{\pm}|^2 = \left[ 1 - \frac{f_2}{f_1} + \left( \frac{f_2}{f_1} \right)^2 \right].
$$

(7.17)

If the two inequivalent atoms are of the same species, $|\Phi_{\pm}|^2 = 1$. In this case the second inequivalent atom does not modify any of the in-plane superstructure intensities, and Patterson function will be the same with or without it.

If the two inequivalent atoms are of different species, the ratio $\frac{f_2}{f_1}$ is real\footnote{Atomic form factor is a real quantity for spherically symmetric atoms and for x-ray wavelengths away from the absorption edges of the atomic species in question.} and depends, in general, on the magnitude of the momentum transfer vector (i.e. $|\vec{q}|$). In cases where this dependence is weak and $|\Phi_{\pm}|^2$ is approximately constant, introduction of the second inequivalent atom does not change the Patterson function \textit{qualitatively} by much. Fig. 7.10 shows that this "weak dependence" condition holds for Au and Sb over a very large range of $|\vec{q}|$.

Consider now a $(3 \times 3)$ surface unit cell with three inequivalent atoms, separated from each other laterally by 2D bulk lattice vectors. As long as the three of them are not all of the same species, the surface has $\left( \sqrt{3} \times \sqrt{3} \right)$ periodicity. By putting the second and third inequivalent atoms respectively $\vec{a}_1$ and $-\vec{a}_1$ from the first, we see that contribution of a type-1 $(3 \times 3)$ surface unit cell to the structure factor of
reflection \((hk0)\) is (Eq. (7.1)):

\[
S_{(hk0)} = [1 + e^{2\pi i(h-k)} + e^{2\pi i(2h-2k)}] f_1 e^{2\pi i h_x} [1 + \frac{f_2}{f_1} e^{2\pi i h} + \frac{f_3}{f_1} e^{-2\pi i h}].
\] (7.18)

Noting the values \(h\) can take, we conclude that introduction of the second and third inequivalent atoms (or rows of atoms,) after some algebra, modifies \(S_{(hk0)}\) by the complex factor:

\[
\Omega_{\pm} = [1 - \frac{f_2 + f_3}{2f_1} \pm i \frac{\sqrt{3}(f_2 - f_3)}{2f_1}].
\] (7.19)

If the three inequivalent atoms are of the same species, this factor becomes zero, the surface no longer has \((\sqrt{3} \times \sqrt{3})\) symmetry. If either the second or third inequivalent atom, or both, are different from the first one, \(|\Omega_{\pm}|^2\) may be approximately constant for some combinations of atomic types or range of momentum transfer vectors, in which case introduction of the second and third inequivalent atoms will not change the Patterson function qualitatively by much. Fig. 7.10 shows that this is the case for the system where the first, second and third inequivalent atoms are taken to be Au, Sb and Sb respectively.
Figure 7.10  Plots of $|\Phi_{\pm}|^2$ and $|\Omega_{\pm}|^2$ (Eqs. (7.16) and (7.19)) as functions of momentum transfer vector magnitude $q = |\vec{q}|$, showing weak dependence over the range of $q$ values of the in-plane superstructure reflections in the present data (indicated by the vertical lines.) For these plots, atoms 1, 2 and 3 are taken to be Au, Sb and Sb respectively.
Chapter 8
Conclusions and Outlook

We have developed a direct method for surface x-ray diffraction (SXRD) based on the Gerchberg-Saxton loop, the object-domain operations of Fienup, and oversampling relative to the Nyquist frequency. The aim of our direct method is to recover the part of a surface structure that is different from the truncated bulk which is assumed to be known. Since both crystal-truncation-rod (CTR) and superstructure-rod (SR) reflections are used, and no assumption is made about atomicity or the rate of change of the phases of the known part of structure factors compared with the unknown part, our direct-method algorithm is robust and is capable of recovering the full atomic structure, not just the average or difference structures.

Our direct-method algorithm has previously been applied on simulated SXRD data and has been shown to work in many different situations.

The efficacy of our method on the experimental front was first proven when we applied it on experimental SXRD data of the clean Au (110) (1 × 2) reconstruction. Our direct method produced a clean 3D image of the electron density distribution where all the previously established structural features could be seen. Using the maxima of this electron density distribution as starting point for conventional refinement, we obtained a final model that agreed very well with previously published models, although none of the previous studies had the ability to detect all the structural fea-
tures. Thus we see that SXRD is a powerful technique for surface structure recovery and that our direct-method algorithm is a powerful tool to produce atomic models for conventional analysis.

The necessity of a direct method that utilizes all measured data was made apparent when we tried to come up with atomic models for the unknown \( c(2 \times 2) \) and \( (\sqrt{3} \times \sqrt{3}) \) phases of Sb/ Au (110) using their fractional Patterson maps. Other than confirming the symmetries of the two systems, these fractional Patterson maps conveyed no extra information. On the other hand, our direct-method algorithm was able to produce clean 3D images of the electron density distributions that enabled us to quickly come up with good atomic models. While some might argue that the final solutions for these two unknown structures were not at all surprising and could have been guessed at eventually, the fact remains that our direct method led us to these structures immediately, without us having to go through the time-consuming and oftentimes frustrating process of refining multiple atomic models.

In the not-too-distant future, the power and robustness of our direct-method algorithm will once again be put to the test as we adapt it for systems with larger surface unit cells (Sb/ Au (110) \( p(5 \times 6) \)) and more complex geometry and symmetry (MgO (111), with \( p3m1 \) symmetry.) In general, the larger and more complex a surface unit cell, the harder it is to interpret its fractional Patterson map or average structure map. In such cases, a direct method that produces clean 3D images of electron density distributions that can be easily interpreted is an invaluable tool that no serious crystallographer should be without.
References


Appendix A

Scattering Amplitudes and Electron Densities

A.1 Derivation of the Fourier Transform relation between Scattering Amplitudes and Electron Densities

The Fourier Transform relation between scattering amplitudes and electron densities will be derived following closely the treatment of Robinson (1991).

When an incident wave of magnitude $A_0$ and wavevector $\vec{k}_0$ is scattered off an electron at $\vec{r}$, amplitude of the scattered wave, as observed a distance $R$ away, is given by the Thomson formula:

$$A_e e^{-2\pi i \vec{k} \cdot \vec{r}} = A_0 e^{-2\pi i \vec{k}_0 \cdot \vec{r}} \frac{q_e^2}{m_e c^2 R},$$  \hspace{1cm} (A.1)

where $A_e$ and $\vec{k}$ are respectively the magnitude and wavevector of the scattered wave, $q_e$ and $m_e$ are the charge and rest mass of an electron, and $c$ is the speed of light in free space.

Defining the momentum transfer vector: $\vec{q} = \vec{k} - \vec{k}_0$, Eq. (A.1) can be written as:

$$A_e = A_0 \frac{q_e^2}{m_e c^2 R} e^{2\pi i \vec{q} \cdot \vec{r}}.$$  \hspace{1cm} (A.2)

If an atom with electron density $\rho(\vec{r}_0)$ about its center $\vec{r}_0 = 0$ is placed at $\vec{r}$, magnitude of the observed scattered x-ray is:

$$A_{atom} = A_0 \frac{q_e^2}{m_e c^2 R} \int \rho(\vec{r}) e^{2\pi i \vec{q} \cdot (\vec{r} + \vec{r}_0)} d^3 \vec{r}_0,$$  \hspace{1cm} (A.3)
\[
\begin{align*}
\text{} &= A_0 \frac{q_e^2}{m_e c^2 R} e^{2\pi i \vec{q} \cdot \vec{r}} f(\vec{q}), \\
\end{align*}
\]  

where

\[
\begin{align*}
f(\vec{q}) &= \int \rho(\vec{r}) e^{2\pi i \vec{q} \cdot \vec{r}} d^3 \vec{r} \\
\end{align*}
\]

is the atomic form factor. Atomic form factor is a real quantity for spherically symmetric atoms and for x-ray wavelengths away from the absorption edges of the atomic species in question.

Putting \( N \) atoms with electron densities \( \rho_j(\vec{r}) \) at \( \vec{r}_j, j = 1, 2, \ldots, N \), to form a basis, magnitude of the observed scattered x-ray takes the form:

\[
\begin{align*}
A_{\text{basis}} &= A_0 \frac{q_e^2}{m_e c^2 R} \sum_{j=1}^{N} \int \rho_j(\vec{r}) e^{2\pi i \vec{q} \cdot (\vec{r}_j + \vec{r})} d^3 \vec{r}, \\
&= A_0 \frac{q_e^2}{m_e c^2 R} \sum_{j=1}^{N} f_j(\vec{q}) e^{2\pi i \vec{q} \cdot \vec{r}_j}, \\
&= A_0 \frac{q_e^2}{m_e c^2 R} F(\vec{q}),
\end{align*}
\]

where

\[
\begin{align*}
F(\vec{q}) &= \sum_{j=1}^{N} f_j(\vec{q}) e^{2\pi i \vec{q} \cdot \vec{r}_j}, \\
&= \sum_{j=1}^{N} \int \rho_j(\vec{r}) e^{2\pi i \vec{q} \cdot (\vec{r}_j + \vec{r})} d^3 \vec{r}
\end{align*}
\]

is the structure factor of this basis.

Finally, if this basis is associated with a 2D lattice to form a crystal with lattice vectors \( \{\vec{a}_1, \vec{a}_2\} \), magnitude of the total scattered x-ray observed at a distance \( R \) away

---

\(^1\)Form factor for each atomic species, as a function of the magnitude of the momentum transfer vector, has been fitted to the function \( f(\vec{q}) = f(q) = \sum_{k=1}^{4} a_k e^{-\frac{\mu_k q^2}{2}} + c \) (Cromer and Waber 1965). The fitting parameters are called Cromer-Mann coefficients.
is given by:

\[ A_{\text{crystal}} = A_0 \frac{q_e^2}{m_e c^2 R} \sum_{j_1=1}^{N_1} \sum_{j_2=1}^{N_2} \sum_{j=1}^{N} \rho_j (\vec{r}) e^{2\pi i \vec{q} \cdot \vec{r}_j + j_1 \vec{a}_1 + j_2 \vec{a}_2} \, d^3 \vec{r}, \quad (A.11) \]

\[ = A_0 \frac{q_e^2}{m_e c^2 R} F (\vec{q}) \sum_{j_1=1}^{N_1} c^{2\pi i j_1 \vec{q} \cdot \vec{a}_1} \sum_{j_2=1}^{N_2} c^{2\pi i j_2 \vec{q} \cdot \vec{a}_2}, \quad (A.12) \]

where \( N_1 \) and \( N_2 \) are respectively the numbers of times the unit cell (with a basis) repeats in the directions specified by \( \vec{a}_1 \) and \( \vec{a}_2 \).

When \( N_1 \) is large, the term \( \sum_{j_1=1}^{N_1} e^{2\pi i j_1 \vec{q} \cdot \vec{a}_1} \), being the sum of many many complex numbers with unit moduli and random phases, is zero unless \( \vec{q} \cdot \vec{a}_1 \) is an integer, in which case it becomes equal to the number of terms in the sum, \( N_1 \). Similarly, when \( N_2 \) is large, the term \( \sum_{j_2=1}^{N_2} e^{2\pi i j_2 \vec{q} \cdot \vec{a}_2} \) is zero unless \( \vec{q} \cdot \vec{a}_2 \) is an integer, in which case it equals \( N_2 \). These are known as Laue conditions, and are satisfied along a diffraction rod. The measured scattering intensity, for large \( N_1 \) and \( N_2 \), is therefore

\[ I = |A_{\text{crystal}}|^2 = A_0^2 \frac{q_e^4}{m_e^2 c^4 R^2} |F (\vec{q})|^2 N_1^2 N_2^2. \quad (A.13) \]

In surface x-ray diffraction (SXRD), the basis would include atoms in both the unknown surface layer and the semi-infinite bulk. In this case \( F (\vec{q}) = S (\vec{q}) + B (\vec{q}) \).

Contribution of the surface layer is given by

\[ S (\vec{q}) = \sum_{j=1}^{N_S} f_j (\vec{q}) e^{2\pi i \vec{q} \cdot \vec{r}_j}, \quad (A.14) \]

where the sum is over all the atoms in a surface unit cell (there are \( N_S \) of them.) The attenuation of x ray must be taken into account when considering the contribution of the semi-infinite bulk. If the amplitude of x ray is taken to be attenuated by a factor \( \exp(-\alpha) \) after passing through a thickness \( a_3 \) of bulk material, then the contribution
of the semi-infinite bulk is given by

\[ B(\vec{q}) = \sum_{j=1}^{N_B} f_j(\vec{q}) e^{2\pi i \vec{q} \cdot \vec{r}_j} \left( 1 + e^{-2\pi i \vec{q} \cdot \vec{a}_3} e^{-\alpha} + e^{-2\pi i \vec{q} \cdot 2\vec{a}_3} e^{-2\alpha} + \ldots \right), \]

\[ = \sum_{j=1}^{N_B} f_j(\vec{q}) e^{2\pi i \vec{q} \cdot \vec{r}_j} \frac{1}{1 - \exp(-2\pi i \vec{q} \cdot \vec{a}_3) \exp(-\alpha)}, \]

\[ = \sum_{j=1}^{N_B} f_j(\vec{q}) e^{2\pi i \vec{q} \cdot \vec{r}_j} \frac{1}{1 - \exp(-2\pi i l) \exp(-\alpha)}, \]  \hspace{1cm} (A.15)

where the sum is over all the atoms in a bulk unit cell (there are \( N_B \) of them.)

If we make the substitution:

\[ \vec{r}_n = \vec{r}_j + \vec{r} \]

in Eq. (A.10),

\[ F(\vec{q}) = \sum_{j=1}^{N} \int \rho_j(\vec{r}_n - \vec{r}_j) e^{2\pi i \vec{q} \cdot \vec{r}_n} d^3\vec{r}_n, \]  \hspace{1cm} (A.17)

\[ = \int u(\vec{r}_n) e^{2\pi i \vec{q} \cdot \vec{r}_n} d^3\vec{r}_n, \]  \hspace{1cm} (A.18)

\[ = FT[u(\vec{r})], \]  \hspace{1cm} (A.19)

where

\[ u(\vec{r}) = \sum_{j=1}^{N} \rho_j(\vec{r} - \vec{r}_j). \]  \hspace{1cm} (A.20)

Thus the set of structure factors \( F(\vec{q}) \) is the Fourier transform of the electron densities \( u(\vec{r}) \) of the basis (Fig. A.1).
A.2 Effects of Thermal Vibration

The electron density distribution of an atom can be described in 1D by the gaussian function:

$$\rho(x) = \frac{\rho_0}{\sqrt{2\pi}\sigma_x} \exp \left[ -\frac{(x - \mu_x)^2}{2\sigma_x^2} \right]. \quad (A.21)$$

This distribution is centered about $x = \mu_x$, has width parameter $\sigma_x$, and is normalized to the total number of electrons $\rho_0$. The Fourier transform of this distribution is given by

$$P(q) = \int_{-\infty}^{\infty} \frac{\rho_0}{\sqrt{2\pi}\sigma_x} \exp \left[ -\frac{(x - \mu_x)^2}{2\sigma_x^2} \right] e^{2\pi i qx} dx = \rho_0 \exp \left(-2\pi^2 q^2 \sigma_x^2\right) \exp(2\pi i q \mu_x). \quad (A.22)$$

If there is an uncertainty associated with the location of the atom due to thermal vibration, that leads to a root-mean-square displacement $\sqrt{\langle (\Delta x)^2 \rangle}$ along the x-direction.

$$2 \int_{-\infty}^{\infty} e^{-\alpha x^2 + \beta x} dx = \sqrt{\frac{\pi}{\alpha}} e^{\frac{\beta^2}{4\alpha}}.$$
axis, then, on average, the electron density is given by
\[
\rho^{T_h}(x) = \frac{\rho_0}{\sqrt{2\pi} \sqrt{\sigma_x^2 + <(\Delta x)^2>}} \exp \left[ -\frac{(x - \mu_x)^2}{2(\sigma_x^2 + <(\Delta x)^2>)} \right], \tag{A.23}
\]
where we have used the superscript \(T_h\) to denote thermal average.

The Fourier transform of this distribution is
\[
P^{T_h}(q) = \rho_0 \exp \left[ -2\pi^2 q^2 (\sigma_x^2 + <(\Delta x)^2>) \right] \exp(2\pi i q \mu_x). \tag{A.24}
\]

The analogous results in 3D are
\[
\rho(\vec{r}) = \rho_0 \frac{1}{\sqrt{2\pi} \sigma_x} e^{-\frac{(x-\mu_x)^2}{2\sigma_x^2}} \times \frac{1}{\sqrt{2\pi} \sigma_y} e^{-\frac{(y-\mu_y)^2}{2\sigma_y^2}} \times \frac{1}{\sqrt{2\pi} \sigma_z} e^{-\frac{(z-\mu_z)^2}{2\sigma_z^2}}, \tag{A.25}
\]
\[
P(\vec{q}) = \rho_0 e^{-2\pi^2 q^2 \sigma_x^2} e^{2\pi i q \mu_x} \times e^{-2\pi^2 q^2 \sigma_y^2} e^{2\pi i q \mu_y} \times e^{-2\pi^2 q^2 \sigma_z^2} e^{2\pi i q \mu_z}, \tag{A.26}
\]
when the atom is fixed in space at \((\mu_x, \mu_y, \mu_z)\) and its electron density distribution has width parameters \(\sigma_x, \sigma_y\) and \(\sigma_z\) respectively in the x-, y- and z- directions, and
\[
\rho^{T_h}(\vec{r}) = \rho_0 \frac{1}{\sqrt{2\pi} \sqrt{\sigma_x^2 + <(\Delta x)^2>}} \exp \left[ -\frac{(x - \mu_x)^2}{2(\sigma_x^2 + <(\Delta x)^2>)} \right] \times \frac{1}{\sqrt{2\pi} \sqrt{\sigma_y^2 + <(\Delta y)^2>}} \exp \left[ -\frac{(y - \mu_y)^2}{2(\sigma_y^2 + <(\Delta y)^2>)} \right] \times \frac{1}{\sqrt{2\pi} \sqrt{\sigma_z^2 + <(\Delta z)^2>}} \exp \left[ -\frac{(z - \mu_z)^2}{2(\sigma_z^2 + <(\Delta z)^2>)} \right], \tag{A.27}
\]
\[
P^{T_h}(\vec{q}) = \rho_0 \exp \left[ -2\pi^2 q^2 (\sigma_x^2 + <(\Delta x)^2>) \right] \exp(2\pi i q \mu_x) \times \exp \left[ -2\pi^2 q^2 (\sigma_y^2 + <(\Delta y)^2>) \right] \exp(2\pi i q \mu_y) \times \exp \left[ -2\pi^2 q^2 (\sigma_z^2 + <(\Delta z)^2>) \right] \exp(2\pi i q \mu_z),
\]
\[
= P(\vec{q}) \exp \left\{ -2\pi^2 q^2 \left[ <(\Delta x)^2> + <(\Delta y)^2> + <(\Delta z)^2> \right] \right\},
\]
\[ \begin{align*}
&= \, P(\vec{q}) \exp \left[ -2\pi^2 q^2 \langle (\Delta r)^2 \rangle \right] = P(\vec{q}) \exp \left( -\frac{1}{4}Bq^2 \right) \tag{A.28} \\
\end{align*} \]

when there is an uncertainty associated with the location of the atom due to thermal vibration. In Eq. (A.28), \( \langle (\Delta x)^2 \rangle \), \( \langle (\Delta y)^2 \rangle \) and \( \langle (\Delta z)^2 \rangle \) are respectively the mean-square displacements of the atom in the x-, y- and z- directions,

\[ \langle (\Delta r)^2 \rangle = \langle (\Delta x)^2 \rangle + \langle (\Delta y)^2 \rangle + \langle (\Delta z)^2 \rangle \tag{A.29} \]

is the total mean-square displacement, and

\[ B = 8\pi^2 \langle (\Delta r)^2 \rangle \tag{A.30} \]

is the *isotropic* Debye-Waller factor\(^3\) (also called Debye-Waller B factor) of the atom.

Thermal vibration thus manifests itself in real space in the broadening of the electron density distribution of an atom (compare Eqs. (A.27) and (A.25)), and in diffraction space in the extra factor \( \exp \left( -\frac{1}{4}Bq^2 \right) \) (Eq. (A.28)). Incorporating this factor into Eqs. (A.15) and (A.14) gives Eqs. (1.7) and (1.8) respectively for the scattering amplitudes of a semi-infinite bulk and a surface layer.

It is also possible to absorb the factor \( \exp \left( -\frac{1}{4}Bq^2 \right) \) into the definition of the atomic form factor:

\[ f^{Th}(\vec{q}) = f(\vec{q}) \exp \left( -\frac{1}{4}Bq^2 \right). \tag{A.31} \]

Eqs. (1.7) and (1.8) then become

\[ B_{\vec{q}} = \sum_j f_j^{Th}(\vec{q}) \exp(2\pi i \vec{q} \cdot \vec{r}_j) \frac{1}{1 - \exp(-2\pi il) \exp(-\alpha)}. \tag{A.32} \]

\(^3\)See Kittel (1987) for a quantum-mechanical treatment of the Debye-Waller factor.
\[ S_{\vec{q}} = \sum_j f_j^{Th}(\vec{q}) \exp(2\pi i \vec{q} \cdot \vec{r}_j). \] (A.33)

**A.3 Average Structure, Difference Structure and Projected Structure**

If a surface reconstructs so that the dimensions of its 2D unit cell (parallel to the surface) are larger than those of the bulk, the integration in Eq. (A.18) must be over a surface unit cell which is the true repeating unit.\(^4\) In the simplest case in which the 2D lattice vectors for the surface are \(\alpha \vec{a}_1\) and \(\beta \vec{a}_2\) where \(\alpha\) and \(\beta\) are positive integers, and \(\vec{a}_1\) and \(\vec{a}_2\) are the 2D lattice vectors for the bulk, Eq. (A.18), for a surface layer with electron densities \(u_s(\vec{r})\), can be written as

\[ S(\vec{q}) = \int_{(\alpha \times \beta)} u_s(\vec{r}) e^{2\pi i \vec{q} \cdot \vec{r}} d^3 \vec{r}, \] (A.34)

where the subscript \((\alpha \times \beta)\) in \(\int_{(\alpha \times \beta)}\) means that the integration is over a 2D area corresponding to a \((\alpha \times \beta)\) array of bulk unit cells.

Eq. (A.34) can also be written as

\[ S(\vec{q}) = \int_{(1 \times 1)} \left[ \sum_{m=0}^{\alpha-1} \sum_{n=0}^{\beta-1} u_s(\vec{R}_{m,n} + \vec{r}) e^{2\pi i \vec{q} \cdot (\vec{R}_{m,n} + \vec{r})} \right] d^3 \vec{r}, \] (A.35)

where the integration is performed over a 2D area corresponding to a bulk unit cell.

\(^4\)Recall that in Eq. (A.18), integration along the direction normal to the surface is always over the full thickness of the structure.
The bulk lattice vector

\[ \vec{R}_{m,n} = m\vec{a}_1 + n\vec{a}_2 \]  

(A.36)

and the double sum \( \sum_{m=0}^{a-1} \sum_{n=0}^{b-1} \) allow us to reach all points inside a surface unit cell from within a bulk unit cell.

If the integration in Eq. (A.35) is performed over a surface unit cell, each and every point within a surface unit cell would be included exactly \( (\alpha \times \beta) \) times. In other words,

\[ (\alpha \times \beta)S(\vec{q}) = \int_{(\alpha \times \beta)} \left[ \sum_{m=0}^{a-1} \sum_{n=0}^{b-1} u_s(\vec{R}_{m,n} + \vec{r}) e^{2\pi i \vec{q} \cdot (\vec{R}_{m,n} + \vec{r})} \right] d^3\vec{r}, \]  

(A.37)

or

\[ S(\vec{q}) = \int_{(\alpha \times \beta)} \left[ \frac{1}{\alpha \times \beta} \sum_{m=0}^{a-1} \sum_{n=0}^{b-1} u_s(\vec{R}_{m,n} + \vec{r}) e^{2\pi i \vec{q} \cdot (\vec{R}_{m,n} + \vec{r})} \right] d^3\vec{r}. \]  

(A.38)

For crystal-truncation-rod (CTR) reflections, \( \vec{q} \cdot \vec{R}_{m,n} \) is an integer. In this case Eq. (A.38) gives

\[ S(\vec{q} \in \vec{q}_{CTR}) = FT [u_{ave}(\vec{r})], \]  

(A.39)

where

\[ u_{ave}(\vec{r}) = \frac{1}{\alpha \times \beta} \sum_{m=0}^{a-1} \sum_{n=0}^{b-1} u_s(\vec{R}_{m,n} + \vec{r}) \]  

(A.40)

is the electron densities of the average structure (also called the folded structure.)

The average structure is obtained by averaging the \( (\alpha \times \beta) \) cells, each of dimensions \( \vec{a}_1 \times \vec{a}_2 \), that make up a surface unit cell, and then stacking copies of the resultant average cell to make a \( (\alpha \times \beta) \) array. Since \( u_S(\vec{r}) \) is always positive, \( u_{ave}(\vec{r}) \) is also always positive.
Applying linearity of the Fourier transform operation on Eqs. (A.34) and (A.39), we obtain

\[ S(\vec{q} \in \vec{q}_{SR}) = FT[u_{\text{diff}}(\vec{r})], \]  

(A.41)

where

\[ u_{\text{diff}}(\vec{r}) = u_{S}(\vec{r}) - u_{\text{ave}}(\vec{r}) \]  

(A.42)

is called the \textit{difference structure}. It is the difference between the surface structure and the average structure. \( u_{\text{diff}}(\vec{r}) \) can have both positive and negative values.

If we take \( \vec{q} = (q_1, q_2, q_3) \) and \( \vec{r} = (r_1, r_2, r_3) \) such that \( \hat{q}_i \cdot \hat{r}_j = \delta_{ij} \), Eq. (A.18) can be written, for a surface layer with electron density distribution \( u_{S}(\vec{r}) \), as

\[ S(q_1, q_2, q_3) = \int u_{S}(r_1, r_2, r_3) e^{2\pi i(q_1r_1 + q_2r_2 + q_3r_3)} \hat{r}_1 \times \hat{r}_2 \cdot \hat{r}_3 \, dr_1 dr_2 dr_3. \]  

(A.43)

Real space vectors are customarily chosen so that \( \hat{r}_1 \) and \( \hat{r}_2 \) are parallel to the surface, and \( \hat{r}_3 \) normal to the surface, in which case

\[ \hat{r}_1 \times \hat{r}_2 \cdot \hat{r}_3 = |\hat{r}_1 \times \hat{r}_2|, \]  

(A.44)

and Eq. (A.43) becomes

\[ S(q_1, q_2, q_3) = \int [\int u_{S}(r_1, r_2, r_3) e^{2\pi i q_3 r_3} \, dr_3] e^{2\pi i(q_1r_1 + q_2r_2)} |\hat{r}_1 \times \hat{r}_2| \, dr_1 dr_2. \]  

(A.45)

Setting \( q_3 = 0 \), this becomes

\[ S(q_1, q_2, 0) = \int u_{\text{proj}}(r_1, r_2) e^{2\pi i(q_1r_1 + q_2r_2)} |\hat{r}_1 \times \hat{r}_2| \, dr_1 dr_2 = FT[u_{\text{proj}}(r_1, r_2)], \]  

(A.46)
where
\[ u_{\text{proj}} (r_1, r_2) = \int u_S (r_1, r_2, r_3) \, dr_3. \]  
(A.47)

We see that scattering amplitudes for the \textit{in-plane} set of momentum transfer vectors\(^5\) are the 2D Fourier transform of the \textit{projected structure} which is obtained by projecting the surface structure onto the plane of the surface.

The important results of this section are summarized in Table A.1.

<table>
<thead>
<tr>
<th>scattering amplitudes</th>
<th>Fourier transform of</th>
<th>Eq. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>full set of ( S (\vec{q}) )</td>
<td>full surface structure</td>
<td>A.34</td>
</tr>
<tr>
<td>( S (\vec{q} \in \vec{q}_{CTR}) )</td>
<td>average structure</td>
<td>A.39</td>
</tr>
<tr>
<td>( S (\vec{q} \in \vec{q}_{SR}) )</td>
<td>difference structure</td>
<td>A.41</td>
</tr>
<tr>
<td>( S (\vec{q} \in { q_3 = 0 }) )</td>
<td>projected structure</td>
<td>A.46</td>
</tr>
</tbody>
</table>

Table A.1 Fourier transform relations between surface scattering amplitudes and surface structures.

\(^5\)In-plane momentum transfer vectors have no out-of-plane components, i.e. \( q_3 = 0 \).
Appendix B
Calculating Attenuation Factors

To find the attenuation factors (or attenuation coefficients) of $N$ attenuators, a minimum of $N+1$ counts must be taken. This is done by measuring the same reflection $N+1$ times, once without any attenuator, and once with each of the attenuators in place ($N$ counts.) The attenuation factors can then be obtained by dividing the latter $N$ counts by the count obtained with no attenuator in place.

Oftentimes this is not adequate nor desirable. As discussed in Sec. 4.2, to use the most sensitive range of our detectors, counts should be kept under about ten thousand per second. On the other hand, counts should be high enough so that uncertainties due to counting statistics are at most a few percents. These considerations are particularly important when determining attenuation factors since these factors will be applied to the full set of data.

In general, $J$ counts involving $K$ different reflections may be measured, with different combinations of attenuators in place. If the attenuation factors of the $M$ attenuators are denoted by $F_m, m = 1, 2, ..., M$, then the counts before attenuation $B_k, k = 1, 2, ..., K$ (not measured) and the counts after attenuation $A_j, j = 1, 2, ..., J$ (measured) are related through:

$$\prod_{m=1}^{M} F^{\phi_{j,m}}_m \prod_{k=1}^{K} B^{\phi_{j,k}}_k = A_j, j = 1, 2, ..., J, \quad (B.1)$$

where $\phi_{j,m}$ is 1 if the $m^{th}$ attenuator is in place when taking the $j^{th}$ count, and 0
otherwise, and $\theta_{j,k}$ is 1 if the $j^{th}$ count is for the $k^{th}$ reflection, and 0 otherwise. For instance, if the 4th count is for the 2nd reflection and with the 1st and 3rd attenuators in place, Eq. (B.1) gives, for this count:

$$F_1 F_3 B_2 = A_4.$$  \hspace{1cm} (B.2)

Taking logarithm on both sides of Eq. (B.1),

$$\sum_{m=1}^{M} \phi_{j,m} \ln (F_m) + \sum_{k=1}^{K} \theta_{j,k} \ln (B_k) = \ln (A_j), j = 1, 2, ..., J,$$ \hspace{1cm} (B.3)

or, in matrix form:

$$
\begin{pmatrix}
\phi_{1,1} & \phi_{1,2} & \cdots & \phi_{1,M} & \theta_{1,1} & \theta_{1,2} & \cdots & \theta_{1,K} \\
\phi_{2,1} & \phi_{2,2} & \cdots & \phi_{2,M} & \theta_{2,1} & \theta_{2,2} & \cdots & \theta_{2,K} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\phi_{J,1} & \phi_{J,2} & \cdots & \phi_{J,M} & \theta_{J,1} & \theta_{J,2} & \cdots & \theta_{J,K}
\end{pmatrix}
\begin{pmatrix}
\ln (F_1) \\
\ln (F_2) \\
\vdots \\
\ln (F_M) \\
\ln (B_1) \\
\ln (B_2) \\
\vdots \\
\ln (B_K)
\end{pmatrix}
= 
\begin{pmatrix}
\ln (A_1) \\
\ln (A_2) \\
\vdots \\
\ln (A_J)
\end{pmatrix}.$$  \hspace{1cm} (B.4)

To be able to solve for the attenuation factors, counts for enough combinations of reflection/attenuator setting must be measured. In particular, the number of measured counts $J$ must be at least as large as the number of unknowns, which is the sum of the number of attenuators $M$ and the number of reflections $K$ involved, i.e. $J \geq M + K$.

If $J = M + K$ and the combinations of reflection/attenuator setting are such
that the matrix on LHS of Eq. (B.4) is nonsingular and thus invertible, then the attenuation factors $F_m, m = 1, 2, ..., M,$ can be uniquely determined.

If $J > M + K$ and the combinations of reflection/attenuator setting are such that the matrix on LHS of Eq. (B.4) can be reduced to an upper echelon form, then the attenuation factors $F_m, m = 1, 2, ..., M,$ can be determined by minimizing the difference between LHS and RHS of Eq. (B.4) using standard least-squares technique.
Appendix C

Other Direct Methods

C.1 Introduction

Three direct methods for surface structure recovery with surface x-ray diffraction (SXRD) are discussed here: Maximum-Entropy Method (MEM), Coherent Bragg Rod Analysis (COBRA) and a Sayre’s Equation based method. These are the methods that I have spent considerable amount of time investigating before finally settling down on the method presented in Chapter 2.

The Maximum-Entropy Method (MEM) looks for the electron density distribution that is most probable given the data and the associated uncertainties. It is the result of an attempt to avoid overfitting of possibly noisy experimental data. MEM is closely related to our direct method based on the Gerchberg-Saxton loop and the Fienup object-domain operations (Ch. 2). Both MEM and our direct method utilize both crystal-truncation-rod (CTR) and superstructure-rod (SR) reflections. MEM is the subject of Sec. C.2.

The Coherent Bragg Rod Analysis (COBRA) method will be introduced in Sec. C.3. It is a graphical method that is based on constructing vector sums on the complex plane. COBRA only works on scattering amplitudes with both a known and an unknown portions, and the variation of the unknown portion along  $l$ \footnote{$l$ is the component of momentum transfer vector normal to the sample surface (Eq. (1.3)).} must be much

\[ \text{114} \]
slower than that of the known portion. These requirements limit the number of systems COBRA can be applied on. In particular, for systems with reconstructed surfaces, COBRA can only be applied to phase the CTR reflections, and therefore only the average structure is recovered (Eq. (A.39)). Some other methods must be applied to phase the SR reflections.

Sayre’s Equation based methods, on the other hand, can only be applied on SR reflections. One such method will be discussed in Sec. C.4, together with an application, in which the CTR reflections are first phased using our direct method.

Also worth mentioning is the direct method of Marks (Marks 1999, Marks et al. 2001). His method assumes that scattering comes from atoms and his algorithm contains elements of maximum entropy, a generalized Sayre’s equation, statistical relationship amongst the unknown phases and a genetic algorithm to search over possible phases. This method will not be discussed in this Appendix.

C.2 Maximum-Entropy Method (MEM)

Maximum-Entropy Method (MEM) originated with the development of the principle of maximum entropy first by Shannon in 1949 in the context of information theory and then by Jaynes in 1957 for use in statistical mechanics. Saldin et al. adapted MEM for recovery of surface atomic structures using SXRD data and successfully applied it on various sets of simulated experimental data: K/Ag(001) (Saldin
et al. 2000), O/Cu(104) and GaAs(111)(2 × 2) (Saldin et al. 2001a). The theory and discussion presented here closely follows the development of the MEM algorithm by Saldin et al. A similar algorithm was proposed by Collins in 1982 for use in protein x-ray crystallography.

When searching for the structural model that best fits a set of experimental SXRD data, one needs to be careful not to succumb to the danger of overfitting the data, which often contains uncertainties and is most likely to be incomplete. Overfitting can often lead to unphysical results.

Instead of looking for the electron density distribution that best fits a set of experimental SXRD data, the Maximum-Entropy Method (MEM) looks for the most probable distribution that is consistent with the data given the associated uncertainties, and in so doing avoids overfitting the data. This is accomplished through the use of Bayesian theorem of conditional probabilities (Sivia 1996), which for our present problem of recovering an electron density distribution \{u\} from a set of measured diffraction data, may be stated as:

\[
\text{Prob}(\{u\}|\text{data}, I) = \frac{\text{Prob}(\text{data}|\{u\}, I) \times \text{Prob}(\{u\}|I)}{\text{Prob}(\text{data}|I)}, \tag{C.1}
\]

where \text{Prob}(A|B) is the probability that A is true given that B is true, and I represents all background information that is assumed to be known.\footnote{If \text{Prob}(A|B) denotes the probability that A is true given that B is true, then the product rule of conditional probability can be written as \text{Prob}(X,Y|I) = \text{Prob}(X|Y,I) \times \text{Prod}(Y|I). Interchanging X and Y gives \text{Prob}(Y,X|I) = \text{Prob}(Y|X,I) \times \text{Prod}(X|I). The two quantities \text{Prob}(X,Y|I) and \text{Prob}(Y,X|I) are obviously identical, thus we obtain \text{Prob}(X,Y|I) \times \text{Prod}(Y|I) = \text{Prob}(Y|X,I) \times \text{Prod}(X|I) or \text{Prob}(X|Y,I) = \text{Prob}(Y|X,I) \times \text{Prod}(X|I)/\text{Prob}(Y|I).}

\text{Prob}(\text{data}|\{u\}, I) is called the likelihood function. It measures the likelihood of
the measured data if the proposed model \( \{ u \} \) is correct and given the background information. \( \text{Prob}(\{ u \}|I) \) is the prior probability. It is the probability that the proposed model \( \{ u \} \) is correct given nothing but the background information. Similarly \( \text{Prob}(\text{data}|I) \), called the evidence, is the probability that the measured data is correct given nothing but the background information. Finally, \( \text{Prob}(\{ u \}|\text{data}, I) \), called the posterior probability, gives the probability that the proposed model \( \{ u \} \) is correct given both the background information and the assumption that the measured data is correct.

Treating all measured data on equal footing, the evidence term can be considered a constant, the posterior probability is then proportional to the product of the likelihood function and the prior probability:

\[
\text{Prob}(\{ u \}|\text{data}, I) \propto \text{Prob}(\text{data}|\{ u \}, I) \times \text{Prob}(\{ u \}|I).
\] (C.2)

Given any model \( \{ u \} \), scattering amplitude \( F^{\text{calc}}_{\vec{q}} \) can be calculated for each momentum transfer vector \( \vec{q} \) of interest. The probability that the experimentally measured scattering amplitude \( F^{\text{obs}}_{\vec{q}} \) (with uncertainty \( \sigma_{\vec{q}} \)) is correct is given by the Gaussian distribution:

\[
\text{Prob}(F^{\text{obs}}_{\vec{q}}|\{ u \}, I) = \frac{1}{\sqrt{2\pi}\sigma_{\vec{q}}} \exp\left(-\frac{|F^{\text{obs}}_{\vec{q}} - F^{\text{calc}}_{\vec{q}}|^2}{2\sigma^2_{\vec{q}}}\right).
\] (C.3)

The likelihood function \( \text{Prob}(\text{data}|\{ u \}, I) \) is therefore given by:

\[
\text{Prob}(\text{data}|\{ u \}, I) = \text{Prob}(\{ F^{\text{obs}}(\vec{q}) \}|\{ u \}, I),
\]

\[
= \prod_{\vec{q}} \text{Prob}(F^{\text{obs}}_{\vec{q}}|\{ u \}, I),
\]
\[ \propto \exp \left( -\frac{1}{2} \sum_{\vec{q}} \left[ \frac{F_{\text{obs}}^\vec{q} - F_{\text{calc}}^\vec{q}}{\sigma^\vec{q}} \right]^2 \right) = \exp \left( -\frac{N}{2} \chi^2 \right) . \tag{C.4} \]

The last result (as well as Eq. (C.3)) requires that \( \{F_{\text{calc}}^\vec{q}\} \) be properly scaled with respect to \( \{F_{\text{obs}}^\vec{q}\} \). (See the description around Eqs. (1.9) and (1.10) for explanation.) In this case, we have

\[ \chi^2 = \frac{1}{N} \sum_{\vec{q}} \left[ \frac{F_{\text{obs}}^\vec{q} - F_{\text{calc}}^\vec{q}}{\sigma^\vec{q}} \right]^2 \tag{C.5} \]

Eq. (C.4) tells us that minimizing \( \chi^2 \) is equivalent to maximizing the likelihood function.

To establish the prior probability, we use standard results applicable to a Boltzmann distribution (Huang 1987) for which the number of ways to distribute \( N \) particles into \( M \) bins with capacities \( \{m\} \) to obtain the distribution \( \{u\} \) is given by:

\[ \Omega = \prod_{i=1}^{M} \frac{m_i^{u_i}}{u_i!} . \tag{C.6} \]

This distribution has an entropy

\[ S = k \ln \Omega = -k \sum_{i=1}^{M} u_i \ln \left( \frac{u_i}{em_i} \right) , \tag{C.7} \]

where \( k \) is the Boltzmann constant.

The probability for the realization of a particular distribution (when only background information is available) is proportional to the number of ways (microstates)

\[ ^3\text{Eq. (1.9) gives } \chi^2 = \frac{1}{N} \sum_{\vec{q}} \left[ \frac{|F_{\text{obs}}^\vec{q}| - |F_{\text{calc}}^\vec{q}|}{\sigma^\vec{q}} \right]^2 \text{ for properly scaled scattering amplitudes. This is equivalent to the definition given here in Eq. (C.5) if we assign the calculated phases to the measured amplitudes, i.e. } F_{\text{obs}}^\vec{q} = |F_{\text{obs}}^\vec{q}| \exp \left[ i \arg \left( F_{\text{calc}}^\vec{q} \right) \right] \forall \vec{q}. \]
the distribution can come about, therefore

\[ \text{Prob}(\{u\}|I) \propto \Omega = \exp \left( \frac{S}{k} \right). \tag{C.8} \]

Substituting Eqs. (C.4) and (C.8) into Eq. (C.2), posterior probability is given by

\[ \text{Prob}(\{u\}|\text{data}, I) \propto \exp \left( \frac{S}{k} - \frac{N}{2} \chi^2 \right). \tag{C.9} \]

To find the most probable electron density distribution that is consistent with the measured diffraction data, we maximize the posterior probability, or equivalently, the argument of the exponential function in Eq. (C.9). This, in turn, is equivalent to maximizing the entropy \( S \) subject to the constraint that \( \chi^2 \) is to be minimized (the constant \( \frac{k}{2} N \) can then be considered a Lagrange multiplier.)

Define

\[ Q[\{u\}] = \frac{1}{k} S[\{u\}] - \frac{N}{2} \chi^2 [\{u\}], \tag{C.10} \]

where \( S \) and \( \chi^2 \) are now written as functionals that depend on the electron density distribution \( \{u\} \), the goal is to find the distribution that satisfies

\[ \frac{\partial Q[\{u\}]}{\partial u_j} = 0 \quad \forall j. \tag{C.11} \]

From Eq. (C.7),

\[ \frac{1}{k} S[\{u\}] = - \sum_{i=1}^{M} u_i \ln \left( \frac{u_i}{e m_i} \right) = - \sum_{i=1}^{M} [u_i \ln(u_i) - u_i - u_i \ln(m_i)], \]

\[ \frac{1}{k} \frac{\partial S[\{u\}]}{\partial u_j} = - [\ln(u_j) + 1 - 1 - \ln(m_j)] = - \ln \left( \frac{u_j}{m_j} \right). \tag{C.12} \]

Writing

\[ F_{\text{obs}}^q = |F_{\text{obs}}^q| e^{i\phi_q}, \tag{C.13} \]
\[ F_{\vec{q}}^{\text{calc}} = B_{\vec{q}} + S_{\vec{q}}[\{u\}] , \]  
\[ \phi_{\vec{q}} \] is the unknown phase associated with the scattering amplitude \( F_{\vec{q}}^{\text{obs}} \), \( B_{\vec{q}} \) and \( S_{\vec{q}}[\{u\}] \) are respectively the bulk and surface layer contribution to \( F_{\vec{q}}^{\text{calc}} \), Eq. (C.5) becomes
\[ \chi^2 \{ \{u\} \} = \frac{1}{N} \sum_{\vec{q}} \frac{\left| F_{\vec{q}}^{\text{obs}} \right| e^{i\phi_{\vec{q}}} - (B_{\vec{q}} + S_{\vec{q}}[\{u\}])}{\sigma^2_{\vec{q}}} \],
Noting that (Eq. (1.6))
\[ S_{\vec{q}}[\{u\}] = \sum_k u_k e^{2\pi i \vec{q} \cdot \vec{r}_k} , \]
\[ \frac{\partial S_{\vec{q}}[\{u\}]}{\partial u_j} = e^{2\pi i \vec{q} \cdot \vec{r}_j} , \]  
Eq. (C.15) can be differentiated with respect to \( u_j \) to give
\[ \frac{\partial \chi^2 \{ \{u\} \}}{\partial u_j} = \frac{1}{N} \sum_{\vec{q}} \left( \frac{\left| F_{\vec{q}}^{\text{obs}} \right| e^{i\phi_{\vec{q}}} - (B_{\vec{q}} + S_{\vec{q}}[\{u\}])}{\sigma^2_{\vec{q}}} \right) e^{-2\pi i \vec{q} \cdot \vec{r}_j} + c.c , \]
\[ = -\frac{2}{N} Re \left[ \sum_{\vec{q}} \left( \frac{\left| F_{\vec{q}}^{\text{obs}} \right| e^{i\phi_{\vec{q}} - (B_{\vec{q}} + S_{\vec{q}}[\{u\}])}}{\sigma^2_{\vec{q}}} \right) e^{-2\pi i \vec{q} \cdot \vec{r}_j} - \sum_{\vec{q}} S_{\vec{q}}[\{u\}] e^{-2\pi i \vec{q} \cdot \vec{r}_j} \right] . \]  
Substituting Eq. (C.10) into Eq. (C.11), then using Eqs. (C.12) and (C.17), we obtain the set of transcendental equations
\[ -\ln \left( \frac{u_j}{m_j} \right) + Re \left[ \sum_{\vec{q}} \left( \frac{\left| F_{\vec{q}}^{\text{obs}} \right| e^{i\phi_{\vec{q}} - B_{\vec{q}}}}{\sigma^2_{\vec{q}}} \right) e^{-2\pi i \vec{q} \cdot \vec{r}_j} - \sum_{\vec{q}} S_{\vec{q}}[\{u\}] e^{-2\pi i \vec{q} \cdot \vec{r}_j} \right] = 0 \quad \forall j , \]
or
\[ u_j = m_j \exp \left( Re \left[ \sum_{\vec{q}} \left( \frac{\left| F_{\vec{q}}^{\text{obs}} \right| e^{i\phi_{\vec{q}} - (B_{\vec{q}} + S_{\vec{q}}[\{u\}])}}{\sigma^2_{\vec{q}}} \right) e^{-2\pi i \vec{q} \cdot \vec{r}_j} - \sum_{\vec{q}} S_{\vec{q}}[\{u\}] e^{-2\pi i \vec{q} \cdot \vec{r}_j} \right) \right) \quad \forall j , \]
which can be solved to obtain the most probable electron density distribution that is consistent with the measured diffraction data.

Instead of solving Eq. (C.19) directly for \( \{u\} \), we will solve it iteratively. To do this, we will make the following assignments/assumptions: (1) \( u_j \) on LHS will become our latest estimate of \( u_j \), i.e. \( u_j \rightarrow u_{j,n} \); (2) \( S_{\vec{q}}[\{u\}] \) and \( \phi_{\vec{q}} \) on RHS will become our estimates of \( S_{\vec{q}} \) and \( \phi_{\vec{q}} \) based on \( \{u\} \) from the last iteration, i.e.

\[
S_{\vec{q}}[\{u\}] \rightarrow S_{\vec{q}}[\{u_{n-1}\}] = S_{\vec{q},n} = \sum_j u_{j,n-1} e^{2\pi i \vec{q} \cdot \vec{r}_j}, \tag{C.20}
\]

and

\[
\phi_{\vec{q}} \rightarrow \phi_{\vec{q},n} = \arg (B_{\vec{q}} + S_{\vec{q},n}); \tag{C.21}
\]

(3) \( \sigma^2_\vec{q} \) on RHS will be replaced by some estimate of the average variance of the data set, i.e. \( \sigma^2_\vec{q} \rightarrow \overline{\sigma^2} \); (4) \( m_j \) on RHS will be replaced by our best estimate of the capacity of “bin” \( j \), which is the electron density from the last iteration, i.e. \( m_j \rightarrow u_{j,n-1} \). Putting these into Eq. (C.19),

\[
u_{j,n} = u_{j,n-1} \exp \left( \frac{1}{\sigma^2} \left[ \sum_\vec{q} \left( |F_{\vec{q}}^{\text{obs}}| e^{i\phi_{\vec{q},n}} - B_{\vec{q}} \right) e^{-2\pi i \vec{q} \cdot \vec{r}_j} - \sum_\vec{q} S_{\vec{q},n} e^{-2\pi i \vec{q} \cdot \vec{r}_j} \right]\right) \quad \forall j,
\]

or

\[
u_{j,n} = u_{j,n-1} \exp \left[ -\lambda (u_{j,n-1} - t_{j,n}) \right] \quad \forall j, \tag{C.22}
\]

where

\[
u_{j,n-1} = \frac{1}{N} \sum_\vec{q} S_{\vec{q},n} e^{-2\pi i \vec{q} \cdot \vec{r}_j}, \tag{C.23}
\]

\[
t_{j,n} = \frac{1}{N} \sum_\vec{q} \left( |F_{\vec{q}}^{\text{obs}}| e^{i\phi_{\vec{q},n}} - B_{\vec{q}} \right) e^{-2\pi i \vec{q} \cdot \vec{r}_j}, \tag{C.24}
\]
and
\[ \lambda = N \sigma^2 \]  
(C.25)
is a positive parameter. The notations and indexing scheme introduced in Sec. 2.3 have been used.

At any iteration \( n > 1 \), Eqs. (C.20),(C.21),(C.24) and (C.22) are iterated to obtain improved estimate of the electron density distribution in the unknown surface layer.

Note that the assignments \( S_\tilde{q}[\{u\}] \rightarrow S_\tilde{q}[\{u_{n-1}\}] = S_{\tilde{q},n} \) and \( \phi_\tilde{q} \rightarrow \phi_{\tilde{q},n} = \arg(B_\tilde{q} + S_{\tilde{q},n}) \) mean that (our estimate of) \( F_{\tilde{q}}^{\text{obs}} \) and \( F_{\tilde{q}}^{\text{calc}} \) always have the same phase, and thus the expression for \( \chi^2 \) (Eq. (C.5)) reduces to the more familiar form
\[ \chi^2 = \frac{1}{N} \sum_\tilde{q} \left[ \frac{|F_{\tilde{q}}^{\text{obs}}| - |F_{\tilde{q}}^{\text{calc}}|}{\sigma_{\tilde{q}}} \right]^2. \]  
(C.26)

Eq. (C.22) has the same input-output feedback structure as the object-domain operations discussed in Sec. 2.2.2, i.e. \( u_{j,n} = f(u_{j,n-1}, t_{j,n}) \) (or \( g_n = f(g_{n-1}, g'_n) \), using the notation in Sec. 2.2.2.) There are two major differences between MEM and iteration schemes based on the Gerchberg-Saxton (GS) loop. In MEM, diffraction-domain constraints are not as rigidly enforced as in GS-type methods. On the other hand, positivity and rigid supports are built into MEM (because of the exponential function in Eq. (C.22), once \( u_j \) has been assigned a positive value, it will stay positive in all subsequent iterations; similarly, if \( u_j \) is assigned a zero value, it will stay zero) whereas in GS-type methods one has the freedom to choose either positivity or rigid supports as the object-domain constraint.

MEM is self-correcting. As convergence is approached, we expect \( \{F_{\tilde{q}}^{\text{obs}}\} \) and
\( \{ F^{\text{calc}}_q \} \) (Eqs. (C.13) and (C.14)), or equivalently \( \{ u_j \} \) and \( \{ t_j \} \) (Eqs. (C.23) and (C.24)), to approach each other. If \( u_j \) is greater than \( t_j \) for some \( j \), then Eq. (C.22) will reduce it in the next iteration (for positive \( \lambda \)); similarly if \( u_j \) is smaller than \( t_j \) for some \( j \), then Eq. (C.22) will increase it in the next iteration. The positive parameter \( \lambda \) in Eq. (C.22) controls the rate of convergence of MEM. If \( \lambda \) is too small, convergence will be very slow. On the other hand, if \( \lambda \) is too large, the algorithm will be very unstable. It has been found (Saldin et al. 2001a) that choosing \( \lambda << 1/\u^{\text{max}}_{n-1} \), where \( \u^{\text{max}}_{n-1} \) is the maximum value of the distribution \( \{ u_{n-1} \} \), ensures the stability of the algorithm.

Two distributions, \( \{ t_1 \} \) and \( \{ u_0 \} \), are needed to initiate MEM. \( \{ t_1 \} \) can be defined by assigning bulk phases to the measured diffraction amplitudes:

\[
\phi_{\vec{q},1} = \arg (B_{\vec{q}}) \quad \forall \vec{q}, \quad \text{(C.27)}
\]

\[
T_{\vec{q},1} = |F^{\text{obs}}_q| e^{i\phi_{\vec{q},1}} - B_{\vec{q}} \quad \forall \vec{q}, \quad \text{(C.28)}
\]

\[
t_1 = FT^{-1} [T_1]. \quad \text{(C.29)}
\]

\( \{ u_0 \} \) can then be defined by enforcing positivity (and perhaps also rigid supports) on \( \{ t_1 \} \). It has been found (Collins 1982, Saldin et al. 2001a) that the assignment:

\[
u_0 = \begin{cases} 
  t_1, & \text{where } t_1 > t_1^{\text{max}}/100 \\
  t_1^{\text{max}}/100, & \text{otherwise}
\end{cases} \quad \text{(C.30)}
\]

where \( t_1^{\text{max}} \) is the maximum value of the distribution \( \{ t_1 \} \), works quite well for many problems. In any case, \( \{ t_1 \} \) and \( \{ u_0 \} \) must be different, or the algorithm will not work.
C.3 Coherent Bragg Rod Analysis (COBRA)

Consider a total scattering amplitude with both surface and bulk contributions, i.e.

\[ F_{\vec{q}} = S_{\vec{q}} + B_{\vec{q}}. \]  

Eq. (C.31) can be represented graphically as vector addition on the complex plane (Fig. C.1 (a)). In Surface X-Ray Diffraction (SXRD), the bulk scattering amplitude \( B_{\vec{q}} \) is known, and if both the magnitude and phase of the total scattering amplitude \( F_{\vec{q}} \) are measured, vectors representing \( B_{\vec{q}} \) and \( F_{\vec{q}} \) can be drawn head-to-head on the complex plane and the vector that connects the tail of \( F_{\vec{q}} \) to the tail of \( B_{\vec{q}} \) represents the surface scattering amplitude \( S_{\vec{q}} \) that we seek.

![Diagram showing vector addition](image)

Figure C.1 (a) Vector diagram showing how \( S_{\vec{q}} \) can be found graphically if both the magnitude and phase of \( F_{\vec{q}} \) are measured. (b) Since only the magnitude (not phase) of \( F_{\vec{q}} \) is experimentally measured, there is an infinite number of solutions for \( S_{\vec{q}} \), each corresponds to a particular choice of the phase of \( F_{\vec{q}} \). Two such choices (denoted by superscripts \( \alpha \) and \( \beta \)) and the corresponding solutions for \( F_{\vec{q}} \) and \( S_{\vec{q}} \) are shown here.
Now since only the magnitude (not phase) of $F_{\bar{q}}$ is accessible in experiment, a circle of radius $|F_{\bar{q}}|$ can be drawn on the complex plane to represent all possible $F_{\bar{q}}$ (Fig. C.1 (b)). Without further information, any vector that starts on the perimeter and ends at the center of this circle is a candidate for $F_{\bar{q}}$. And if we plot $B_{\bar{q}}$ so that it ends at the center of this circle, then any vector that starts on the perimeter of the circle and ends at the tail of $B_{\bar{q}}$ is a candidate for $S_{\bar{q}}$. Two possible pairs of $F_{\bar{q}}$ and $S_{\bar{q}}$ are shown in Fig. C.1 (b) but there is actually an infinite number of candidate pairs.

The number of candidate pairs reduces to two, at the most, if there are two total scattering amplitudes:

\begin{align*}
F_1 &= S_1 + B_1, \quad \text{(C.32)} \\
F_2 &= S_2 + B_2 \quad \text{(C.33)}
\end{align*}

for which

\begin{equation}
S_1 = S_2. \quad \text{(C.34)}
\end{equation}

To see this, vectors representing $B_1$ and $B_2$ are drawn so that their tails are at the origin of the complex plane (Fig. C.2). Circles of radii $|F_1|$ and $|F_2|$ are then drawn respectively about the heads of $B_1$ and $B_2$. Now since $S_1$ must start on the perimeter of the circle with radius $|F_1|$ and end at the tail of $B_1$, and $S_2$ must start on the perimeter of the circle with radius $|F_2|$ and end at the tail of $B_2$, only the vectors that start at the intersections (if any) of the two circles and end at the origin of the complex plane satisfy Eq. (C.34). Fig. C.2 shows the case when this COBRA construction (Sowwan et al. 2002) gives two candidate solutions.
Figure C.2 COBRA construction (Sowwan et al. 2002) for the solution of Eqs. (C.32), (C.33) and (C.34) with known $B_1$, $B_2$, $|F_1|$ and $|F_2|$: $B_1$ and $B_2$ are drawn so that their tails are at the origin of the complex plane. Circles of radii $|F_1|$ and $|F_2|$ are then drawn respectively about the heads of $B_1$ and $B_2$. Vectors that start at the intersections (if any) of the two circles and end at the origin of the complex plane are candidates for $S(=S_1=S_2)$. Depending on the number of intersection points between the two circles, there may be zero, one or two candidate solutions. The two-solution case is shown here, with superscripts $\alpha$ and $\beta$ denoting the two candidate solutions. This rather complex figure is broken down in Fig. C.3 to show more clearly the vector additions.
Figure C.3 Vector additions in the COBRA construction of Fig. C.2: (a) $F_1^\alpha = S^\alpha + B_1$; (b) $F_2^\alpha = S^\alpha + B_2$; (c) $F_1^\beta = S^\beta + B_1$; (d) $F_2^\beta = S^\beta + B_2$. 
Eq. (C.34) should be approximately true for scattering amplitudes at two diffraction-space points that are sufficiently close to one another, in which case the COBRA construction is still valid. In particular, Sowwan et al. (2002) argues that if diffraction intensities along each crystal truncation rod are sampled frequently enough (i.e. $\Delta l$ small enough,) Eq. (C.34) would be approximately true, and COBRA construction can be performed, for scattering amplitudes at any two consecutive diffraction-space points (or $l$ points) sampled along the same rod. Between the two candidate solutions in each COBRA construction, the one that leads to a smaller change in $S$, going from one $l$ point to the next, is chosen, in accordance with our approximation that Eq. (C.34) is true.

Fig. C.4 shows typical results of a successful application of the COBRA method along a crystal truncation rod. The results shown here are for a simulated set of data so the correct phases of both the bulk and the surface layer are known. These phases are plotted as functions of $l$ in the left panel. It is no coincidence that the phase of the bulk (known part of the structure) varies much faster, as a function of $l$, than the phase of the surface layer (unknown part of the structure.) This, in fact, is necessary for the approximation in Eq. (C.34) to be valid (Sowwan et al. (2002)). The center panel shows how the phases of the COBRA solutions for $S$ (COBRA phases) separate neatly into two series when plotted as a function of $l$. The series that varies more slowly is the one that more closely satisfies Eq. (C.34). The right panel shows that this slow series of COBRA phases agree very well with the correct phases.

---

4If phase derivatives are experimentally accessible, then another version of the COBRA method (Yacoby et al. 2000) can be used that does not require the phase variation of the known part of the scattering amplitudes to be much faster than that of the unknown part.
Figure C.4 (Color) Typical COBRA results. Left panel: Phases of the bulk $\phi_B$ and surface layer $\phi_S$ plotted as functions of $l$. Center panel: Phases of the COBRA solutions plotted as functions of $l$. The phases separate into two series, a \textit{slow-varying} one and a \textit{fast-varying} one. Right panel: The \textit{slow-varying} series of COBRA phases and the correct phases of the surface layer plotted as functions of $l$, showing good agreement between them.

Since COBRA construction only works for scattering amplitudes with both a known and an unknown part (bulk and surface contributions in our case,) it can only be applied on crystal truncation rods and not superstructure rods. For systems with reconstructed surfaces, some other methods must be applied to obtain the phases of the superstructure reflections.

The requirement that the phase of the bulk (the known part) must vary much faster, as a function of $l$, than the phase of the surface layer (the unknown part) limits the kind of structures that can be analyzed with the COBRA method. Our experience shows that in order for the COBRA method to give the correct results, the phase of the known bulk must vary as least five to ten times as fast, as a function of $l$, as the phase of the unknown surface layer. We will now show that most surface structures do not meet this requirement.
The bulk and surface scattering amplitudes respectively take the forms:

\[
B_{\vec{q}} = \sum_j u_B(\vec{r}_j) \exp(2\pi i\vec{q} \cdot \vec{r}_j)/[1 - \exp(-2\pi il) \exp(-\alpha)], \tag{C.35}
\]

\[
S_{\vec{q}} = \sum_j u_S(\vec{r}_j) \exp(2\pi i\vec{q} \cdot \vec{r}_j) \tag{C.36}
\]

where \(u_B\) and \(u_S\) are respectively the electron densities of the bulk and surface unit cells, and the sums are over all the atoms in a bulk (for \(B_{\vec{q}}\)) or surface (for \(S_{\vec{q}}\)) unit cell. \(\alpha\) is the attenuation coefficient for x-ray in the crystal bulk and the factor \(1/[1 - \exp(-2\pi il) \exp(-\alpha)]\) is the result of summing up the contributions of all the bulk layers. If we consider the very common situation where the vertical extent of the surface layer is roughly the same as the height of a bulk unit cell, the sums in Eqs. (C.35) and (C.36) both vary as \(\exp(2\pi il)\) if we put the origin at the bulk/surface interface.\(^5\) Noting that the factor \(1/[1 - \exp(-2\pi il) \exp(-\alpha)]\) also varies roughly as \(\exp(2\pi il)\), we conclude that

\[
\phi_B \sim 4\pi l, \tag{C.37}
\]

\[
\phi_S \sim 2\pi l, \tag{C.38}
\]

where \(\phi_B\) and \(\phi_S\) are respectively the phases of the bulk and the surface layer, and the symbol \(\sim\) means “varies as.” The phase variation, as a function of \(l\), is therefore only twice as fast for the bulk amplitudes as for the surface amplitudes when the vertical extent of the surface layer is roughly the same as the height of a bulk unit cell.

\(^5\)Putting the origin elsewhere changes the algebra slightly but does not change the final conclusion for this case.
The COBRA method is more suitable for analysis of interface structures than surface structures. For systems where a thin unknown layer is sandwiched between identical known structures, the phase variation of the known part of the scattering amplitude, as a function of $l$, becomes faster as more layers of the known structure are deposited. For instance, if $m$ monolayers of the bulk material are deposited on top of the surface structure described above (Fig. C.5), scattering amplitude of the known part gains an extra term:

$$
\sum_j u_B(\vec{r}_j) \exp\left(2\pi i \vec{q} \cdot \vec{r}_j \right) \frac{1 - \exp(-2\pi il) \exp(-\alpha)^m}{1 - \exp(-2\pi il) \exp(-\alpha)} \exp[2\pi i (m+1)l], \quad (C.39)
$$

and becomes

$$
B_\vec{q} = B_\vec{q} \{1 - [\exp(-2\pi il) \exp(-\alpha)]^m \} \exp[2\pi i (m+1)l], \quad (C.40)
$$

The phase of the known part of the scattering amplitude thus varies roughly as $2\pi (m+3)l$ ($4\pi l$ from the bulk (Eq. (C.37)) and $2\pi (m+1)l$ from the top layer (Eq. (C.40)).

For interface structures where a thin unknown layer is sandwiched between identical known structures, and where the top layer is sufficiently thick, the COBRA method should work.

Another situation for which COBRA might work is if the phase variation of the unknown scattering amplitudes is much slower than $\phi_S \sim 2\pi l$. In particular, if the vertical extent of the surface layer is $\frac{1}{m}$ the height of a bulk unit cell, then the phases of the unknown part of the scattering amplitudes vary as $\phi_S \sim \frac{2\pi l}{m}$.

In applying COBRA method, it is possible to incorporate a model for the surface/
Figure C.5  (a) A surface system. For the common situation where the vertical extent of the surface layer is roughly the same as the height of a bulk unit cell, COBRA does not work.  (b) An interface system formed by depositing bulk material on top of the surface system in (a). COBRA works for this interface system if the top layer is sufficiently thick.

interface layer into the known part of the structure, the unknown part will then be the difference between the true surface/ interface structure and the model. In this case, as long as the phases of the known part (bulk + model) vary much faster, as functions of $l$, than the phases of the unknown part (difference between the true surface/ interface structure and the model), the COBRA construction should be valid.

Finally, the basic COBRA construction discussed above can be turned into an iteration scheme. At the end of each COBRA run, the new estimates of the unknown scattering amplitudes can be transformed into electron densities in real space, some kind of object-domain operations (e.g. supports constraint) (Sec. 2.2.2) can be applied, and the resultant electron densities can be used to generate a new model to be incorporated into the known part of the structure, and the process repeats.
Despite its limitations, the COBRA method has been successfully applied over the years. Yacoby et al. (2000, 2002) solved the layer structure of an experimental interface system where four monolayers of AlAs were sandwiched between a GaAs (110) substrate and a top layer of twenty monolayers of GaAs. Sowwan et al. (2002) determined the structure of thin films of Gd$_2$O$_3$ epitaxially grown on GaAs (100) starting with a model that was based on the structure of bulk Gd$_2$O$_3$ (110). In the first case, only the specular rod (i.e. (00l)) was analyzed, so only the heights of the atomic layers were recovered. In the second case, the unknown layer had bigger 2D unit cells than the known part, so only the average structure was recovered using the COBRA construction.

C.4 A Sayre’s Equation Based Method

To arrive at Sayre’s Equation (Sayre 1952), two approximations/ assumptions need to be made. The first one is atomicity where the electron densities of any two atoms in our system are assumed to be well separated and not overlap significantly. Under this assumption, the atomic form factor (Eq. (A.5)) for atom $k$ at $\vec{r}_k$ becomes

$$f_k (\vec{q}) = \int_{k} u_S (\vec{r}) \exp \left[ 2\pi i \vec{q} \cdot (\vec{r} - \vec{r}_k) \right] d^3 \vec{r}, \quad (C.41)$$

where $u_S (\vec{r})$ is the electron density in a unit cell of the surface layer, and the subscript $k$ in $f_k$ means that the integration is over a small neighborhood of $\vec{r}_k$. 
Eq. (A.33) is repeated here for easy reference, and without the superscript\(^6\) \(T_h\), as Eq. (C.42):

\[
S_{\vec{q}} = \sum_k f_k(\vec{q}) \exp(2\pi i\vec{q} \cdot \vec{r}_k). \quad \text{(C.42)}
\]

Substituting Eq. (C.41) into Eq. (C.42) gives

\[
S_{\vec{q}} = \sum_k \int_k u_S(\vec{r}) \exp (2\pi i\vec{q} \cdot \vec{r}) d^3\vec{r}. \quad \text{(C.43)}
\]

Performing integrations in the neighborhoods of all the atoms in a unit cell and then adding up the results is equivalent to performing one integration over the entire unit cell, i.e. \(\sum_k f_k = f\), therefore the scattering amplitude of the surface layer becomes

\[
S_{\vec{q}} = \int u_S(\vec{r}) \exp (2\pi i\vec{q} \cdot \vec{r}) d^3\vec{r}, \quad \text{(C.44)}
\]

which is just the continuous version of the inverse of Eq. (1.6).

When the electron density in a unit cell of the surface layer is \(u_S^2(\vec{r})\), the analogous results to Eqs. (C.41), (C.42) and (C.44) are

\[
g_k(\vec{q}) = \int_k u_S^2(\vec{r}) \exp \left[2\pi i\vec{q} \cdot (\vec{r} - \vec{r}_k)\right] d^3\vec{r}, \quad \text{(C.45)}
\]

\[
G_{\vec{q}} = \sum_k g_k(\vec{q}) \exp(2\pi i\vec{q} \cdot \vec{r}_k) \quad \text{(C.46)}
\]

and

\[
G_{\vec{q}} = \int u_S^2(\vec{r}) \exp (2\pi i\vec{q} \cdot \vec{r}) d^3\vec{r}. \quad \text{(C.47)}
\]

\(^6\)For this section, it is assumed that all thermal vibration effects have been properly taken care of. See Sec. A.2 for details.
The scattering amplitudes $S_{\vec{q}}$ and $G_{\vec{q}}$ are related, as

$$
\sum_{\vec{q}} S_{\vec{q}} S_{\vec{q} - \vec{q}'} = \sum_{\vec{q}} \int u_S (\vec{r}) \exp \left( 2\pi i \vec{q} \cdot \vec{r} \right) d^3 \vec{r} \cdot \int u_S (\vec{r}') \exp \left[ 2\pi i (\vec{q} - \vec{q}') \cdot \vec{r}' \right] d^3 \vec{r}',
$$

$$
= \int \int u_S (\vec{r}) u_S (\vec{r}') \exp \left( 2\pi i \vec{q} \cdot \vec{r} \right) \sum_{\vec{q}'} \exp \left[ 2\pi i \vec{q}' \cdot (\vec{r} - \vec{r}') \right] d^3 \vec{r} d^3 \vec{r}',
$$

$$
= N \int u_S^2 (\vec{r}) \exp \left( 2\pi i \vec{q} \cdot \vec{r} \right) d^3 \vec{r} = N G_{\vec{q}}
$$

where $N$ is the number of momentum transfer vectors in the sum, and we have used normalization:

$$
\sum_{\vec{q}'} \exp \left[ 2\pi i \vec{q}' \cdot (\vec{r} - \vec{r}') \right] = N \delta (\vec{r} - \vec{r}') \tag{C.49}
$$

and Eqs. (C.44) and (C.47) for $S_{\vec{q}}$ and $G_{\vec{q}}$.

Now we invoke the *equal-atom approximation*\(^7\) where all the atoms in our system are assumed to be of the same species. Under this assumption, $f_k (\vec{q})$ (Eq. (C.41)) and $g_k (\vec{q})$ (Eq. (C.45)) are related through a real constant\(^8\) that is independent of the atom index $k$:

$$
\frac{f_k (\vec{q})}{g_k (\vec{q})} = \theta_{\vec{q}}. \tag{C.50}
$$

Substituting Eq. (C.50) into Eq. (C.42), then using Eq. (C.46), we see that the scattering amplitudes $S_{\vec{q}}$ and $G_{\vec{q}}$ are related through the same constant:

$$
S_{\vec{q}} = \sum_k \theta_{\vec{q}} g_k (\vec{q}) \exp (2\pi i \vec{q} \cdot \vec{r}_k) = \theta_{\vec{q}} G_{\vec{q}}. \tag{C.51}
$$

Eliminating $G_{\vec{q}}$ between Eqs. (C.48) and (C.51), we obtain

$$
S_{\vec{q}} = \frac{\theta_{\vec{q}}}{N} \sum_{\vec{q}'} S_{\vec{q}} S_{\vec{q} - \vec{q}'} \tag{C.52}
$$

---

\(^7\)Equivalently, we could invoke the *average-atom approximation* where each and every atom in our system is replaced by an average atom.

\(^8\) $f_k (\vec{q})$ and $g_k (\vec{q})$ are real if atom $k$ is spherically symmetric.
which is the famous Sayre’s equation relating scattering amplitudes. Taking arguments of both sides of Eq. (C.52), remembering that \( \theta_{\vec{q}} \) is real, we obtain

\[
\arg(S_{\vec{q}}) = \arg \left( \sum_{\vec{q}'} S_{\vec{q}'} S_{\vec{q} - \vec{q}'} \right).
\]  

(C.53)

Eq. (C.53) is sometimes known as a tangent formula. It can easily be turned into an iteration scheme for improving estimates of the unknown phases of the surface scattering amplitudes:

\[
\arg(S_{\vec{q}}^{(n+1)}) = \arg \left( \sum_{\vec{q}'} S_{\vec{q}'}^{(n)} S_{\vec{q} - \vec{q}'}^{(n)} \right).
\]  

(C.54)

Direct methods based on Sayre’s Equation (Eq. (C.52)) can only be used on surface scattering amplitudes since there is no easy way to handle the sum-to-infinity factor that appears in the bulk scattering amplitudes. Also, since the surface contribution to crystal-truncation-rod (CTR) reflections cannot be separated out without first solving the structure, the tangent formula iteration scheme (Eq. (C.54)) can only be used on superstructure-rod (SR) reflections.

Saldin et al. (2003) combined the tangent formula iteration scheme (Eq. (C.54)) with our direct method based on the Gerchberg-Saxton loop and the Fienup object-domain operations (Ch. 2) into a two-step process for surface structure recovery, and successfully applied it on a set of simulated experimental SXRD data to recover the projected structure of a hypothetical \( c(2 \times 2)K/TiO_2(001) \) structure.

In this two-step method, the magnitudes and phases of the surface scattering amplitudes of the CTR reflections are first recovered using our direct method. These surface scattering amplitudes (both magnitudes and phases) then go on RHS of
Eq. (C.54), i.e. they are held fixed and are not updated. SR reflections are initially assigned random phases and they go on both sides of Eq. (C.54). Each pass through the iteration scheme updates the phases of the SR reflections while keeping their experimentally measured magnitudes unchanged. The set of values to which these phases converge are then taken as the phases of the SR reflections.
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Publications
