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Crystallographic Image Processing with Unambiguous 2D Bravais Lattice
Identification on the Basis of a Geometric Akaike Information Criterion

by

Taylor Thomas Bilyeu

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science
in
Physics

Thesis Committee:
Peter Moeck, Chair
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Portland State University
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Abstract

Crystallographic image processing (CIP) is a technique first used to aid in the structure determination of periodic organic complexes imaged with high-resolution transmission electron microscopes (TEM). The technique has subsequently been utilized for TEM images of inorganic crystals, scanning TEM images, and even scanning probe microscope (SPM) images of two-dimensional periodic arrays. We have written software specialized for use on such SPM images. A key step in the CIP process requires that an experimental image be classified as one of only 17 possible mathematical plane symmetry groups. The current methods used for making this symmetry determination are not entirely objective, and there is no generally accepted method for measuring or quantifying deviations from ideal symmetry. Here, we discuss the crystallographic symmetries present in real images and the general techniques of CIP, with emphasis on the current methods for symmetry determination in an experimental 2D periodic image. The geometric Akaike information criterion (AIC) is introduced as a viable statistical criterion for both quantifying deviations from ideal symmetry and determining which 2D Bravais lattice best fits the experimental data from an image being processed with CIP. By objectively determining the statistically favored 2D Bravais lattice, the determination of plane symmetry in the CIP procedure can be greatly improved. As examples, we examine scanning tunneling microscope images of 2D molecular arrays of the following compounds: cobalt phthalocyanine on Au

(111) substrate; nominal cobalt phthalocyanine on Ag (111); tetraphenoxyphtalocyanine on highly oriented pyrolytic graphite; hexaazatriphenylene-hexacarbonitrile on Ag (111). We show that the geometric AIC procedure can unambiguously determine which 2D Bravais lattice fits the experimental data for a variety of different lattice types. In some cases, the geometric AIC procedure can be used to determine which plane symmetry group best fits the experimental data, when traditional CIP methods fail to do so.

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Abbreviations

1D	One-dimension
2D	Two-dimensions
3D	Three-dimension
AFM	Atomic force microscope
AIC	Akaike information criterion
CIP	Crystallographic image processing
CTF	Contrast transfer function
DFT	Discrete Fourier transform
EDM	Electron Direct Methods
FFT	Fast Fourier transform
FT	Fourier transform
HRTEM	High resolution transmission electron microscope
ITC	International Tables for Crystallography
IUCr	International Union of Crystallography
POA	Phase object approximation
PSF	Point spread function
SPM	Scanning probe microscope
STM	Scanning tunneling microscope
TEM	Transmission electron microscope
VEC	Visual Electron Crystallography
WPOA	Weak phase object approximation

1 Overview

We begin this text by systematically building up the theory of crystallographic symmetry, as it pertains to real two-dimensional (2D) periodic images. This includes translation and point symmetries, and their combination in the form of the 17 crystallographic plane symmetry groups. We then run through the very basics of the Fourier transform (FT), beginning with the continuous transform in one dimension (1D) and ending once again with a manifestation pertinent to real 2D periodic images, the 2D discrete fast FT (FFT). Through some examples, we examine the importance of the phase and magnitude of complex numbers which make up the FT of an image. With the basics of crystallographic symmetry and the FT covered, we introduce the technique of crystallographic image processing (CIP) which relies heavily on such concepts. The general steps of CIP, especially as carried out in our own CIP software, are detailed. Next, imaging in a transmission electron microscope (TEM) and a scanning tunneling microscope (STM) are compared to illustrate the differences in the application of CIP for both types of images. The use of traditional figures of merit (such as phase residuals) to determine plane symmetry in an experimental image (a key step in CIP) is described, and illustrated with screen captures from several popular CIP computer programs. The geometric Akaike information criterion (AIC) allows us to improve upon the symmetry determination procedure generally used in CIP. We adapt a procedure from the robotics community (which classifies an experimental shape as one of the regular quadrilaterals using the geometric AIC)

to determine which 2D Bravais lattice is most likely present in an experimental image. As examples, we use the geometric AIC to help determine (on a statistically sound basis) the plane symmetry present in several STM images of 2D molecular arrays: tetraphenoxypthalocyanine on graphite, cobalt phthalocyanine on Au (111) and cobalt phthalocyanine on Ag (111). In the case of tetraphenoxypthalocyanine on graphite, we verify our conclusion through the CIP analysis of a higher quality image of the same sample.

2 Symmetry

2.1 Crystals

Most non-crystallographers would define a crystal as a periodic arrangement of atoms in three-dimensional space (3D). However, the seemingly elementary question “what is a crystal?” has in fact been a source of contention in the crystallographic community for some time. In 1991, the International Union of Crystallography (IUCr) had this to say about the matter [1]:

“by ‘crystal’ we mean any solid having an essentially discrete diffraction diagram”

This definition hardly ended the debate, as its arbitrary nature, in particular the phrase ‘essentially discrete’, has left many unsatisfied. In 2007, the question was once again brought to the attention of the community, and some interesting discussion ensued [2–8], resulting in some consensus that the following definition be used:

1. A crystal is a solid that has long-range positional order
2. Long range positional order can be inferred from the existence of Bragg peaks in the Fourier spectrum of the solid.

Unfortunately, this definition suffers from a similar problem in that the inference of long range positional order is somewhat subjective. Today, the following definition of a crystal by the IUCr is not much different than that given in 1991 [9]:

“A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering.”

For the purpose of clarity in expressing the ideas this paper, it is convenient to make a distinction between an ideal crystal and a real crystal. An ideal crystal is a purely mathematical entity, with exact translational and local or global rotational symmetry. Such a crystal does not truly exist in nature. Real crystals are finite in extent, contain defects such as dislocations and vacancies, and are not exactly symmetric. However, ideal crystals are very useful for describing and understanding real crystals. In fact, real crystals are closely modeled by ideal crystals, and small deviations from the ideal case can be essentially averaged out over the entire crystal, such that a real crystal, for all intents and purposes, behaves as if it were ideal.

With all of the above in mind, we take the naive approach and define a crystal as a solid whose atoms are arranged periodically in 3D space. Due to this periodicity, a crystal can be seen as being composed of identical parts, each of which is known as a unit cell. The unit cell of a particular crystal is somewhat arbitrary. In an ideal crystal, there are an infinite number of possible unit cells, but in practice, a unit cell

which is as highly symmetric as possible according to crystallographic conventions is chosen.

The entire crystal structure can be built up by repeating the unit cell in several directions. Therefore, one need only know the periodicity of the unit cell and the arrangement of atoms within the unit cell to completely describe a crystal. This can greatly reduce the work involved for many applications. To elucidate the usefulness of treating a real crystal as an ideal one, consider that a crystal sample containing hundreds or thousands of unit cells can be described with a just a single one of them. An example of a 3D unit cell, as well as the common notation for the parameters used to describe it (known as lattice parameters) is shown in Figure 2.1.

2.2 Crystal Symmetry

Symmetry is a fundamental property of a crystal. The symmetry of a crystal can be defined in terms of its symmetry elements and symmetry operations. Symmetry elements are points and lines (2D), or points, axes and planes (3D) about which a symmetry operation (such as translation, rotation, reflection and inversion) is performed. Symmetry operations are transformations under which an object is invariant. They are a special case of Euclidian mapping. The symmetry of a crystal is of great importance. Besides reducing the work done in describing the crystal itself, the symmetry of physical properties (and phenomena) of a crystal is inherited from the symmetry of the crystal itself [10, 11].

For instance, consider a crystal in some type of field. Curie's Principle says that

FIGURE 2.1: The unit cell of a crystal in 3D is a parallelepiped, defined by three lattice vectors a , b , and c , and three lattice angles α , β and γ . A crystal is composed of translations of the unit cell along integer multiples of the lattice vectors.

symmetries present in the causes (crystal and field) must be present in the effects (crystal+field), and also that asymmetries in the effects must be present in the causes. Thus, the symmetry of a crystal under the influence of some external field will have at least the symmetries which are common to both the crystal without the field and the field without the crystal:

$$G_{\text{crystal+field}} \supseteq G_{\text{crystal}} \cap G_{\text{field}} \quad (2.1)$$

where G here stands for symmetry group. Additionally, Curie’s Principle acts as a constraint for predicting the unknown symmetry of a cause. For instance, by observing the crystal+field system, we gain some insight into the internal symmetry of the crystal itself.

2.3 Translation Symmetry

The periodicity of the unit cell is referred to as translation symmetry, and this is usually represented with a crystal lattice. The lattice is a mathematical construct that helps us visualize and describe symmetry. In a crystal or an image, the neighborhood around the points of a lattice (lattice points) should be identical to all other lattice points. An example of a partial lattice for a 2D pattern is shown in Figure 2.2 with lattice points in green.

What may not yet be apparent here is that the lattice points correspond to integer multiples of the lattice vectors that define the unit cell, as well as their linear combinations. That is, if the lattice vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ from Figure 2.1 are linearly independent and form a basis for 3D Cartesian space, the corresponding lattice is defined as the set of all integral linear combinations of those lattice vectors,

$$t = u_1\mathbf{a} + u_2\mathbf{b} + u_3\mathbf{c} \tag{2.2}$$

where u_i are integers [13]. Thus, the lattice is a useful mathematical tool for visualizing both the shape and the periodicity of the unit cell in a crystal. However, the lattice alone tells us nothing about the positioning of actual atoms or molecules

FIGURE 2.2: Image of 2D pattern with partial lattice overlaid (green dots in the color version are ‘lattice points’). The pattern surrounding one of the lattice points (its neighborhood) is identical to that of all other lattice points. This pattern was generated with the free online Java applet Escher Web Sketch [12].

within the crystal. A generic example of a 2D unit cell and the corresponding lattice is shown in Figure 2.3. Notice that in this case, we only have three lattice parameters: $\mathbf{a}$, $\mathbf{b}$ and γ .

2.4 Point Symmetry

The possible symmetry operations compatible with a crystal lattice are limited to rotations, inversion and combinations of the two. The inversion symmetry operation is performed about a symmetry element known as the inversion point. If the inversion point is at the origin, the inversion operation maps a point (x, y, z) onto the point

FIGURE 2.3: Relation between a lattice, unit cell and lattice parameters in 2D. This is a ‘primitive’ unit cell, as it contains only one lattice point per cell (1/4 of a point at each corner).

$(-x, -y, -z)$. Rotoinversion involves a rotation operation, followed by the inversion operation. Similarly, rotoreflection involves performing a rotation operation, followed by a reflection operation across a mirror plane; these all result in transformations that are redundant with rotoinversions. Rotorelections are generally limited to use with the Schoenflies notation, whereas the preferred notation of the International Tables for Crystallography is the Hermann-Mauguin notation [14]. The non-translational symmetry operations compatible with a crystal are shown below in Table 2.1, along with the common symbols for the associated symmetry element.

A unique combination of one or more of the operations in Table 2.1 constitutes a

TABLE 2.1: Crystallographic Symmetry Operations of a Crystal

Rotation	Symbol	Rotoinversion	Symbol
1-fold (360°)	1	1-fold inversion	$\bar{1}$
2-fold (180°)	2	2-fold inversion	$m(\text{mirror})$
3-fold (120°)	3	3-fold inversion	$\bar{3}$
4-fold (90°)	4	4-fold inversion	$\bar{4}$
6-fold (60°)	6	6-fold inversion	$\bar{6}$

crystallographic point group (a non-crystallographic point group could contain rotations of any angle). A point group is a group of symmetry operations under which an object is invariant about a point [15]. In our case, the object of interest is usually a 2D periodic image. In 2D there are only 10 possible point groups. The point group of a crystal is associated with many physical properties, such as piezoelectricity, ferroelectricity and optical activity, to name a few. All possible 2D crystallographic point groups, along with the symmetry elements associated with them are listed in Table 2.2.

2.5 Two-Dimensional Bravais Lattices

If one were to attempt to combine the crystallographic point symmetries of the previous section with the lattices (translation symmetry) described in Section 2.3, they would find that we are restricted to a set of special lattices. These lattices arise due to the fact that an object cannot have point symmetry and be translated to tile space except for very specific translations. These are the so-called ‘Bravais lattices.’ In 2D, there are only five Bravais lattices, which each belong to one of four ‘crystal systems’,

TABLE 2.2: Crystallographic Point Groups in 2D

Symbols used	Unique symmetry elements
1	1
2	1, 2
m	1, m
3	1, 3
4	1, 2, 4
6	1, 2, 3, 6
$2mm$	1, 2, two mirrors
$3m$	1, 3, three mirrors
$4mm$	1, 2, 4, four mirrors
$6mm$	1, 2, 3, 6, six mirrors

The International Tables for Crystallography also differentiate between certain elements such as 4^+ and 4^- being counter-clockwise and clockwise rotations of 90 degrees. Additionally, $3m$ is split into $3m1$ and $31m$, two different variations of the same point group but with different matrix representations.

which in turn belong to a ‘crystal family’. The crystallographic point groups belong to only one crystal system. Within a crystal system, the crystallographic point group which has the symmetry of the corresponding lattice (lattice point symmetry), is referred to as the holohedral point group for that lattice, or ‘holoedries’ in the plural form [16]. Other point groups within a crystal system are subgroups of the corresponding holohedral point groups. A summary of the Bravais lattices and their corresponding crystal family, crystal system, point groups and holohedral groups is given in Table 2.3.

For 4 of the 5 2D Bravais lattices, a ‘primitive’ unit cell, containing only one lattice point, is used. The symbols for these lattices are ‘ mp ’, ‘ op ’, ‘ tp ’ and ‘ hp ’. The first letter identifies the crystal family to which the Bravais lattice belongs (see Figure

2.4) and the second letter p indicates that a primitive unit cell is used. The fifth Bravais lattice is described by a non-primitive ‘centered’ cell containing two lattice points per unit cell. The centered cell is preferred over the primitive one for this type of Bravais lattice because the full symmetry becomes apparent. This type of lattice belongs to the rectangular crystal system (orthorhombic crystal family) and so it is designated by the symbol ‘ oc ’, to distinguish it from the Bravais lattice ‘ op ’, which shares the same crystal class and family. In common usage (and in the rest of this work), the 2D Bravais lattices can be referred to by their crystal system designation rather than their symbols from Table 2.3. So Bravais lattice types mp , op , oc , tp and hp become oblique, rectangular (or rectangular primitive), centered (or rectangular centered), square and hexagonal, respectively. Each Bravais lattice is illustrated in Figure 2.4, along with the corresponding unit cell. Both the primitive and centered

Crystal family	Symbol	Crystal system	Crystallographic point groups	Bravais lattices
<i>Two dimensions</i>				
Oblique (monoclinic)	m	Oblique	1, $\boxed{2}$	mp
Rectangular (orthorhombic)	o	Rectangular	m , $\boxed{2mm}$	op oc
Square (tetragonal)	t	Square	4, $\boxed{4mm}$	tp
Hexagonal	h	Hexagonal	3, 6 $3m$, $\boxed{6mm}$	hp

TABLE 2.3: Bravais lattice symbols and their corresponding crystal family and crystal system. The crystallographic point groups belong to a crystal system are also shown. Holohedral point groups for a given lattice are outlined. (Table modified from [14]).

cells are shown for a centered lattice.

FIGURE 2.4: The five Bravais lattice types in 2D. The symbol designations given by the IUCr are given in (in parenthesis), as well a common designation determined by their crystal class. The unit cells for each type of lattice are also shown, including restrictions on the lattice parameters. For a rectangular centered lattice, both the primitive (1 lattice point) and centered (2 lattice points) unit cells are shown.

2.6 The 17 Plane Symmetry Groups

The results of combining the symmetry operations of the 2D point groups with the 2D Bravais lattices (translation symmetries) are known as the plane symmetry groups. They are also sometimes called ‘wallpaper groups’ for obvious reasons, or 2D ‘space groups’, in reference to the more general result of combining all possible crystallographic point groups with the 3D Bravais lattices.

A plane symmetry group describes the symmetry of an infinitely repeating pattern in 2D. Any such pattern must be associated with one and only one of the plane symmetry groups. As was the case for the 2D point groups and the 2D Bravais lattices, there are a finite number of these groups, 17 to be precise. These 17 groups are illustrated in Figure 2.5 in the same manner as reference [14], in terms of the shape of the unit cell and the positions of symmetry elements for any pattern associated with one of these groups.

The Hermann-Mauguin notation is again used to designate these groups. A p or c is used to denote whether the group is associated with a primitive or a centered unit cell. The first number represents the highest order of rotational symmetry (if there is any) in the group. Finally, an m or a g is used to denote the existence of mirror lines or glide lines. Analogously to the point groups (Table 2.2), plane groups $p3m1$ and $p31m$ represent a different orientation of the mirror line.

Also, we note that these plane symmetry groups are only compatible with the particular 2D Bravais lattice used to generate them. One could probably glean such relationships from Figure 2.5, but it will be useful later on to have outlined these relationships specifically. We do so in Figure 2.6.

The 17 Plane Symmetry Groups

FIGURE 2.5: The 17 plane symmetry groups.

FIGURE 2.6: 17 plane symmetry groups, grouped by color (grayscale) according to their corresponding 2D Bravais lattice.

3 The Fourier Transform

3.1 Terminology

The idea of the Fourier transform (FT) was first introduced by Joseph Fourier in the 19th century [17]. Since then, it has been used extensively in many different areas of science, mathematics and engineering. As such, there is a wide variety of different notations, representations and terminology used, depending on the particular application and what the variables actually represent.

In this section and throughout this paper, we used a notation that is as consistent as possible with that typically used in the crystallographic community, while hopefully avoiding confusion in describing the one-dimensional, two-dimensional, continuous and discrete cases. We are chiefly concerned with the FT of images, and we generally refer to data in the original image existing in ‘real space’ and that of the transformed image existing in its dual ‘reciprocal space’.

3.2 Continuous Fourier Transform

In general, the FT is an integral operation that transforms a function of a complex (or less generally, a real) variable $f(x)$ into a function of a different complex variable $F(k)$. A common representation of the FT of $f(x)$ is given below:

$$F(k) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i k x} dx. \quad (3.1)$$

A key property of the FT is the symmetry which allows the original function $f(x)$ to be obtained by applying the inverse transform on $F(k)$:

$$f(x) = \int_{-\infty}^{\infty} F(k) e^{2\pi i k x} dk. \quad (3.2)$$

The functions f and F above are commonly referred to as Fourier pairs, and the dual variables x and k can be said to occupy a space (real) and its dual (reciprocal) space, respectively.

3.3 Discrete Fourier Transform

Based on the appropriate use of sampling and distribution theory, it is possible to derive the one-dimensional (1D) discrete Fourier transform (DFT) as a special case of the 1D continuous transform [18]. In notation analogous to that used for the continuous transforms from above, we have the DFT and the inverse DFT:

$$F(k) = \sum_{n=0}^{N-1} f(x_n) e^{2\pi i \left(\frac{nk}{N}\right)} \quad (3.3)$$

$$f(x) = \frac{1}{N} \sum_{n=0}^{N-1} F(k_n) e^{-2\pi i \left(\frac{nx}{N}\right)} \quad (3.4)$$

where x_n is a set of N discrete values at which the original function $f(x)$ is sampled, and k_n is the corresponding set of N discrete values in the domain of $F(k)$.

One should note that to transform a set of N data points (or equivalently transform a function which has been sampled at N points) requires N complex multiplications

and a summation of N terms, giving it a complexity of order $O(N^2)$. For very large sample sizes, this is quite prohibitive even when one considers the power of modern computer processors. This limitation can be overcome through the use of a Fast Fourier Transform [19, 20].

3.4 Fast Fourier Transform

The Fast Fourier Transform (FFT) is a blanket term which encompasses a plethora of algorithms which are each individually capable of computing the DFT more efficiently than a straightforward computation using the definition given in Equations (3.3) and (3.4). Indeed, a typical FFT algorithm has complexity of order $O(N\log_2 N)$. For most applications of the FFT, the computational savings are huge.

One disadvantage of most FFT's is that the size of the data sets to be processed must be a power of 2. These are typically referred to as radix-2 FFT algorithms, such as the widely used Cooley-Turkey algorithm [19]. Split-radix [21, 22] and prime factor [23] algorithms have also been popular. Although there are many different types of FFT algorithms available, some of which will work with other data sizes, it is safe to say that the bulk of FFTs, or at the very least those which are used most often, will work best with a power of 2 data size. For periodic data in particular, it is often convenient to reduce the number of points used in the computation to a power of 2 rather than implement a different algorithm altogether.

3.5 Two-Dimensional Transform

In two dimensions (2D), the continuous FT pair takes the following form:

$$F(h, k) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y) e^{2\pi i(xh+yk)} dx dy \quad (3.5)$$

$$f(x, y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} F(h, k) e^{-2\pi i(xh+yk)} dh dk \quad (3.6)$$

As was the case in 1D, the DFT pair in 2D can be derived as a special case of the continuous FT. A transform of this nature requires, predictably, a double sum:

$$F(h, k) = \sum_{x=0}^{N-1} \sum_{y=0}^{M-1} f(x, y) e^{2\pi i \left(\frac{xh}{N} + \frac{yk}{M} \right)} \quad (3.7)$$

$$f(x, y) = \frac{1}{NM} \sum_{h=0}^{N-1} \sum_{k=0}^{M-1} F(h, k) e^{-2\pi i \left(\frac{xh}{N} + \frac{yk}{M} \right)} \quad (3.8)$$

The 2D transform also suffers from computational inefficiency, even more so than the 1D case. Luckily, it is fairly straightforward to implement the same FFT algorithms as those used in 1D. The fact that the FT is separable allows us to compute the DFT in 2D as a sequence of (M+N) 1D transforms. For example, if the input data is represented as an N x M matrix, one can first calculate a 1D transform for each of the N columns to create an intermediate N x M matrix. Next, additional 1D transforms are calculated for each of the M rows of the intermediate matrix, yielding a final N x M matrix which accurately represents the 2D DFT. Of course, each of the associated 1D transforms should be calculated with a FFT algorithm for optimal computational

efficiency.

3.6 Fourier Transforms in Our Software

The FT is a vital part of our software, and CIP in general. It is therefore of importance to understand precisely how the FT is implemented. MATLAB's 'fft2' function is used to do a standard 2D DFT by performing 1D transforms on the columns followed by the rows (or vice versa) as described above. Additionally, MATLAB's implementation of the FFTW library is used [24]. This enables a tuning algorithm to determine the most efficient FFT (and hence inverse FFT) computation for a specific data size, as well as computer architecture and store the result for that session. When processing a single image with CIP, at least 1 FFT and 16 inverse FFT computations are needed to generate the 16 possible 'symmetrized' images with one of the plane symmetry groups enforced. Since all such computations are based on the same original image (or image area), the FFT size is the same. This means that the overall computation time for processing a single image can be greatly reduced.

4 The Importance of Phase and Magnitude in the Fourier Transform

It is a well-established fact that for many applications, the FT phase is more important than the magnitude [25, 26]. A variety of approaches have been used to justify the importance of phase on FT analysis in general [27, 28]. In [25] and [26], various images are compared with their magnitude-only and phase-only reconstructions, as well as a mix of the two, to demonstrate this importance. Similar examples are presented here for illustration.

Figure 4.1a is a portrait of this author's graduate advisor. Figures 4.1b and 4.1c show the magnitude-only and phase-only reconstructions, respectively. The magnitude-only image is the result of an inverse-FFT which uses the Fourier coefficient magnitudes of the original image with a constant phase (zero). The phase-only image on the other hand, uses the Fourier coefficient phases of the original image with a constant magnitude (unity). Obviously, the phase image bears a close resemblance to the original. Indeed, most of the important local information necessary for image reconstruction, the positions of edges in the image for instance, are contained within the phases. Meanwhile, the magnitude image bears no resemblance to the original, so far as the eye can tell.

Figure 4.2 repeats another example from [26], in which the FT magnitudes and phases from two images (the portrait from Figure 4.1a and Portland State University's logo) are mixed. Figure 4.2c was constructed with the phases from the portrait and the

FIGURE 4.1: (a-top) Image of this author's graduate advisor. (b-left) Inverse FFT using FT magnitudes from (a) and constant phase of zero. (c-right) Inverse FFT using FT phases from (a) and constant magnitude of unity. These are the so called 'magnitude only' and 'phase only' Fourier transforms. Information on edge locations, etc. is contained in the FT phases.

magnitudes from the logo, while Figure 4.2d was constructed with the phases from the logo and the magnitudes from the portrait. In both cases the features of the resulting reconstruction identify with the original from which the phase was taken much more so than the original from which the magnitude information was taken.

FIGURE 4.2: (a-top left) Portrait of this author's graduate advisor. (b-top right) Portland State University's logo. (c-bottom left) Inverse FT using the phases from (a) and the magnitudes from (b). (d-bottom right) Inverse FT using the phases from (b) and the magnitudes from (a). In both cases, to the human eye the image identifies more closely to the image from which its phases were taken.

These examples confirm the importance of phases in reconstructing an image from its Fourier coefficients, but they do not tell the whole story. Since we are primarily concerned with CIP, we repeat the above example using a periodic image. In Figure 4.3, we once again use the portrait from the previous examples as one of the originals (Figure 4.3a). In Figure 4.3b however, we now have a periodic image of a layer of fluorinated cobalt phthalocyanine (F_{16}CoPc) molecules on highly oriented pyrolytic graphite, taken with a scanning tunneling microscope under ultra-high vacuum at the Technical University of Chemnitz [29, 30]. Figure 4.3c utilizes the phase from the portrait and the magnitude from the periodic image, while Figure 4.3d uses the phases from the periodic image and the magnitude from the portrait.

Interestingly, we see that Figure 4.3d does not clearly display characteristics of either of the original images. On the other hand, Figure 4.3c, which was constructed with the magnitudes of the periodic image and the phase information from the portrait, bears some resemblance to both of the originals. We get the same type of edge information from the phases of the portrait as in previous examples, but it appears that the periodic nature of Figure 4.3b (i.e. the lattice information) is contained within the FT magnitudes, which would explain why Figure 4.3d bore no resemblance to the originals.

This result may be surprising at first, but one should consider the properties of the FT. Fourier phases are relative to a particular origin, and a translation of one unit cell is equivalent to a phase change of 360° . If a periodic object is translated, the FT phases are unchanged given an appropriate choice of origin. Figure 4.3b clearly has

FIGURE 4.3: (a-top left) Portrait of this author's graduate advisor. (b-top right) STM image of $F_{16}CoPc$ molecules on highly oriented pyrolytic graphite, taken at the Technical University of Chemnitz under ultra-high vacuum at 20 Kelvin, with a tungsten tip, 1V tip bias and 0.1 nA tunneling current [29, 30]. (c-bottom left) Inverse FT using phases from (a) and magnitudes from (b). (d-bottom right) Inverse FT using phases from (b) and magnitudes from (a).

translation symmetry in two directions. It is therefore plausible to assume that while the phases contain local information about the image (such as the shape of a single molecule), they do not contain information about the positions of those molecules (periodicity) as generated by translation of that molecule in the image. Indeed, the phase-only FT has been used to ‘remove periodicity’ from images for the purpose of defect and irregularity detection [\[31\]](#).

For our purposes in this paper, we will put some emphasis on using the FT magnitudes for symmetry determination in CIP. This is complimentary to the typical symmetry determination procedures in CIP which emphasize the FT phases, as will be discussed later.

5 Crystallographic Image Processing

5.1 Introduction

CIP as a whole is a fairly straight forward technique. The basic steps are described succinctly in the following quote by Nobel Prize winner and CIP pioneer Sir Aaron Klug [32]:

“The essence of image processing of this type is that it is a two-step procedure after the first image has been obtained. First the Fourier transform of the raw image is produced. Next, Fourier coefficients are manipulated, or otherwise corrected, and then transformed back again to reproduce the reconstructed image.”

This is of course a very elementary description, but should give the reader a solid impression of what the technique entails. In fact, it is similar to the examples of Chapter 4 in that we (1) take the FT of a raw image, (2) manipulate the FT coefficients (magnitude and phase), and then (3) reconstruct the corrected image from these new coefficients. The only major difference here is the way in which we manipulate the coefficients.

5.2 A CIP Program for the SPM Community

We are in the process of developing a CIP computer program for the SPM community consisting of several modules which roughly correspond to the three steps described

above: (1) the lattice indexing module, (2) the coefficient symmetrization module, and (3) the image reconstruction module. All 3 modules are included in the program Tools for SPM based CIP (T4SC).

5.2.1 Obtaining and Indexing the Lattice

This module is responsible for importing the raw image, calculating the DFT of the raw image, and storing the result in a format which allows the user to properly manipulate the FT coefficients in the next module.

Users have the opportunity to import images of various file formats. Digital images in the RGB color format are automatically converted to grayscale images (color will not be preserved in the FT). The grayscale intensity of each pixel in an $M \times S$ input image is then stored as a real integer value in an $M \times S$ matrix. The user can then select a circular or square region of interest, whose dimensions are $2^n \times 2^n$, where $n = \{8, 9, 10, 11\}$. A circular region is usually preferred to reduce streaking and other edge effects in the FT. Various window functions, such as the Hann function [18], are available to reduce aliasing type effects. The resulting pixel information is then stored in an $N \times N$ matrix, where $N = 2^n$, as chosen earlier.

We're now ready to carry out the FT. As mentioned in Section 3.6, the FFTW library [24] is utilized to determine the most efficient FFT algorithm for calculating the DFT. The result, as described in Section 3.5 and 3.6, is an array of complex numbers, consisting of phase and magnitude, which are stored in two separate $N \times$

N matrices. The Fourier magnitudes are then displayed as an $N \times N$ grayscale image with pixel intensity equal to the square of the corresponding matrix element.

In Chapter 4, we covered the importance of FT magnitudes in a periodic image [31]. In fact, the symmetry of the real space image is closely related to the symmetry of the Fourier coefficients [33]. Recall Equation (2.2), which defines a lattice in terms of integral linear combinations of the three lattice vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. Similarly, in reciprocal space we have a corresponding reciprocal lattice defined by the vectors $\mathbf{r}^*$:

$$\mathbf{r}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (5.1)$$

where h , k and l are integers and $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the reciprocal lattice vectors. In 2D, the two lattices are related by the following dot products:

$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = 1 \quad (5.2)$$

$$\mathbf{a}^* \cdot \mathbf{b} = \mathbf{b}^* \cdot \mathbf{a} = 0 \quad (5.3)$$

Notice that the magnitudes of the reciprocal lattice vectors are inversely proportional to their real space counterpart. One should also be aware of the fact that the units are inverted: if the length of $\mathbf{a}$ is in cm or pixels in real space, then the length of $\mathbf{a}^*$ is in cm^{-1} or pixels^{-1} in reciprocal space. The most important result however, is the fact that, if the lattice in reciprocal space is known, the unit cell shape and lattice in the real space image can be determined.

From Equation (5.1), we expect the magnitudes in reciprocal space to be periodic in 2D according to the indices h and k . That is, for a perfect, infinitely periodic image, we should get a perfectly discrete FT magnitude map, with peaks at positions (h, k) in reciprocal space, and zero magnitude everywhere else. To find the reciprocal lattice vectors, we use a standard peak search algorithm on the matrix containing the FT magnitudes. This is intended to isolate the peaks at positions (h, k) and filter out low intensity or erroneous peaks resulting from irregularities in the image or imperfections in the FFT algorithms. Once this is accomplished, integer values (h, k) are assigned to the remaining peaks by an indexing algorithm, or manually by the user.

If done properly, the lattice vectors $\mathbf{a}^*$ and $\mathbf{b}^*$ should point from the origin to $(1, 0)$ and $(0, 1)$, respectively, and the final lattice parameter, γ^* , is simply the angle between the two vectors. Figure 5.1 is a screenshot of our lattice indexing module, illustrating the indexing of the FT magnitudes.

5.2.2 Symmetrizing the Coefficients

Once the DFT has been indexed, the next step is the symmetrization of the FT coefficients. This is accomplished by forcing the symmetry of one of the 17 plane symmetry groups onto the coefficients. Enforcing the lowest symmetry group, $p1$, amounts to translation averaging over all of the unit cells in the raw image. Enforcing the 16 higher symmetry groups is a bit more involved. For instance, the group $p3$ has a 3-fold rotation axis at the origin of the unit cell. To enforce $p3$, any observed FT magnitudes, $|F_{\text{obs}}(h\ k)|$, related to each other by 120° rotations about the 3-fold

FIGURE 5.1: Simulated image with $p4mm$ symmetry. (right) Screenshot of the lattice indexing module of our CIP software. The indexing of the FT magnitudes from the image on the left (square lattice and unit cell) is illustrated. Approximately 1/4 of the FT magnitudes are shown. The reciprocal lattice parameters given in the ‘Lattice parameters’ panel can be used to determine the unit cell in real space using Equation (5.2).

axis, are changed to the average of the three values, $|F_{\text{sym}}(hk)|$. This is repeated for all symmetry elements of the symmetry group.

The symmetrized phase for symmetry related coefficients is calculated as the phase of the resultant vector from summation of all such coefficients:

$$\phi_{\text{sym}}(hk) = \tan^{-1} \left[\frac{\sum_i |F_{i,\text{obs}}(hk)| s_i \sin(\phi_{i,\text{obs}}(hk))}{\sum_i |F_{i,\text{obs}}(hk)| s_i \cos(\phi_{i,\text{obs}}(hk))} \right] \quad (5.4)$$

where the index i denotes the i th coefficient in the set of symmetry related coefficients, and s is either 1 or -1 depending on the group being enforced. For centrosymmetric groups, $\phi_{\text{sym}}(hk)$ is then set to either 0° or 180° , whichever is closer [34].

Both the phase and magnitude is unchanged for reflections that are not symmetry related; that is, $\phi_{\text{sym}}(h k) = \phi_{\text{obs}}(h k)$ and $|F_{\text{sym}}(h k)| = |F_{\text{obs}}(h k)|$. For a given symmetry element, one can determine the indices of symmetry equivalent coefficients, (h', k') , by multiplying the original indices (h, k) by the rotation matrix associated with the operation, followed by the addition of any translation vector associated with centered groups or glide planes (reference [34] pages 53-58).

Finally, we should note again that Fourier coefficient phases are relative to the origin chosen. To choose an origin, a phase residual is introduced. This is a distance measure that quantifies how much the phases of the symmetrized coefficients deviate from the experimental ones (discussed in more detail in Chapter 7). Observed and symmetrized phases, as well as the corresponding phase residual are calculated relative to an origin at every point within the unit cell. The position which minimizes the phase residual is chosen as the origin, and the symmetrized phases resulting from this particular origin are used. The phase origin map from our CIP software, which displays the phase residual for different choices of origin within the unit cell, is illustrated in Figure 5.2.

The phases relative to a new origin can be easily calculated by due to the fact that a single period should correspond to 360° . Therefore a shift of origin from $(0, 0)$ to $(1/4, 5/6)$ in fractional coordinates of the unit cell, for instance, is equivalent to a phase change of $(90^\circ, 300^\circ)$. The total phase change would then be given by the following formula:

$$\phi_{(1/4, 5/6)}(h k) = \phi_{(0, 0)}(h k) + h \cdot 90^\circ + k \cdot 300^\circ \quad (5.5)$$

FIGURE 5.2: Screenshot of the phase origin map from our software. Global phase residual minima are seen in the top right and bottom left corners (dark blue in the color version of this paper). Calculating phases relative to an origin placed at these locations results in the lowest phase residuals (smallest deviation of phases between experimental and symmetrized images).

5.2.3 Reconstructing the Image

Once the FT coefficients have been symmetrized by enforcing a plane symmetry group on the original image, an inverse FFT is performed to generate the corrected image in real space. An image can be defined as the convolution ($\otimes$) of the true object being imaged (ideal image) and the point spread function (PSF) of the imaging instrument, which is responsible for any kind of distortion or deviation from the true object in

the image. That is,

$$i(x, y) = o(x, y) \otimes p(x, y) \quad (5.6)$$

where i is the image, o is the ideal image and p is the PSF. If we take the Fourier transform of both sides of Equation (5.6), the convolution becomes a simple multiplication and we get the following relation, where I , O and P are the FT of i , o and p , respectively:

$$I(h, k) = O(h, k) P(h, k) \quad (5.7)$$

Assuming that the object being imaged is a known highly symmetric calibration standard, the FT of the point spread function (and hence the point spread function itself) can be calculated using the following equation:

$$P(h, k) = \frac{I(h, k)}{O(h, k)} \quad (5.8)$$

For our purposes, I is simply the unsymmetrized FT coefficients for the raw image, and O is the symmetrized coefficients after enforcing the known symmetry of the calibration standard. Knowledge of the PSF and its FT (gleaned from a calibration standard) allows us to calculate the ideal image o for an unknown sample without any prior knowledge and without performing CIP again. Of course, this is only valid if the conditions under which the unknown sample is imaged are very close to those under which the calibration standard was imaged. For scanning probe microscopy, this technique amounts to determining the ‘effective tip’, which includes both the tip shape and other imaging induced distortions. A more detailed discussion of the

concepts discussed here, as well as examples of PSF determination using CIP can be found in reference [\[29\]](#).

6 Imaging in TEM and STM

6.1 Introduction

In this chapter, we discuss briefly the primary imaging tools/techniques to which CIP is applied, TEM and STM. We focus on STM due to the microscope’s ability to image large arrays of periodic molecules at molecular or even atomic resolution, making it very amenable to an averaging technique like CIP. However, conclusions about STM, in regards to CIP, should also be applicable to other forms of scanning probe microscopes, such as atomic force microscopy (AFM), for example. The purpose of discussing these imaging techniques here is to highlight differences in the application of CIP to both types of images and provide some motivation for slight modifications to the standard symmetry determination procedure in CIP.

In the case of TEM, a variety of software packages have been developed over the years for the analysis of commensurate and incommensurate inorganics as well as for quasi-2D membrane forming proteins [35–38]. As for STM, this kind of microscope has not traditionally been considered to be a crystallographic instrument. However, recent work shows that one may indeed consider STMs that image regular 2D arrays as useful tools for the assessment of 2D surface crystallography [29, 30, 39, 40]. Many concepts from HRTEM image based crystallography are directly applicable to such a surface crystallography approach.

6.2 Imaging in TEM

Since its advent in 1912, the field of x-ray crystallography has been enormously successful in terms of analyzing and determining the structure and properties of crystalline materials. However, there are limitations to x-ray diffraction techniques. For instance, a crystal may be too small to be studied with single-crystal x-ray diffraction due to the weak interaction between matter and x-rays. In such cases, electron diffraction is often a viable technique, due to the much stronger interaction between matter and electrons. Unfortunately, for both x-ray and electron diffraction, structure factor phase information (i.e. projected electrostatic potential of the crystal) is lost when the diffraction pattern is collected [41–43]. However, when the electrons in a TEM are focused to obtain a phase contrast HRTEM image of the sample rather than a diffraction pattern, the structure factor phase information is adequately preserved. For this reason, HRTEM has become a vital tool for structural analysis. Indeed, the primary role of CIP in TEM is to correct for distortions of these phases to aid in structure determination. Before this is possible though, one must know how the FT phases from the HRTEM image relate to the actual electrostatic potential of the sample.

Parallel beams are traditionally used to illuminate the sample for TEM imaging. An electron in the TEM beam can be treated as a plane wave with constant amplitude and phase, which then interacts with the electrostatic potential of the sample. The wavelength of the electron inside the crystal is determined by the electrostatic

potential of the crystal, $\varphi(\mathbf{r})$, and the accelerating voltage of the electron beam, V :

$$\frac{1}{\lambda_{\text{eff}}} = \frac{1}{\lambda} \sqrt{1 + \frac{\varphi(\mathbf{r})}{V}} \quad (6.1)$$

$$\approx \frac{1}{\lambda} \left(1 + \frac{\varphi(\mathbf{r})}{V} \right) \quad (6.2)$$

The above approximation is valid because the accelerating voltage is much greater than the electrostatic potential of the crystal. From this we determine that the differential phase shift for an electron passing through a sample layer of thickness dt is

$$d\phi = \frac{2\pi}{\lambda_{\text{eff}}} dt - \frac{2\pi}{\lambda} dt \quad (6.3)$$

After integrating, we find the total phase change is then,

$$\Delta\phi = \frac{2\pi me\lambda}{h^2} \varphi_z(\mathbf{r}) \quad (6.4)$$

$$= \sigma \varphi_z(\mathbf{r}) \quad (6.5)$$

where σ is the interaction constant, $\varphi_z(\mathbf{r})$ is the projected electrostatic potential along the z direction, h is Planck's constant, and m and e are the relativistic mass and charge of the electron, respectively.

If we assume that absorption effects are negligible and that only the electron phase (and not the amplitude) is affected by interaction with the crystal, then the specimen

transfer function, $f(\mathbf{r})$, is given as follows:

$$f(\mathbf{r}) = \exp(-i\sigma\varphi_z(\mathbf{r})) \quad (6.6)$$

This is the phase object approximation (POA). The POA is only valid if the electrons are elastically scattered nearly parallel to the incident wave. This is equivalent to Fraunhofer diffraction [44]. Expanding Equation (6.6) in a Taylor series, we get:

$$f(\mathbf{r}) = 1 - i\sigma\varphi_z(\mathbf{r}) - \frac{\sigma^2}{2}(\varphi_z(\mathbf{r}))^2 + i\frac{\sigma^3}{6}(\varphi_z(\mathbf{r}))^3 + \dots \quad (6.7)$$

If a sample is extremely thin, such that the projected potential $\varphi_z(\mathbf{r}) \ll 1$, we can ignore higher order terms in Equation (6.7) and use the so called weak phase object approximation (WPOA) for the specimen transfer function,

$$f(\mathbf{r}) = 1 - i\sigma\varphi_z(\mathbf{r}). \quad (6.8)$$

Assuming that the incident electron wave has constant phase and amplitude, $\psi_0(\mathbf{r}) = 1$, then under the WPOA, the electron wave at the exit surface of the sample is given as,

$$\psi_{\text{exit}}(\mathbf{r}) = \psi_0(\mathbf{r}) f(\mathbf{r}) \quad (6.9)$$

$$= 1 - i\sigma\varphi_z(\mathbf{r}) \quad (6.10)$$

Assuming that the incident electron wave has constant phase and amplitude, $\psi_0(r) = 1$, then under the WPOA, the electron wave at the exit surface of the sample is given as,

$$\psi_{exit}(\mathbf{r}) = \psi_0(\mathbf{r}) f(\mathbf{r}) \quad (6.11)$$

$$= 1 - i\sigma\varphi_z(\mathbf{r}) \quad (6.12)$$

So we see that the amplitude of the electron wave function at the exit surface is linearly related to the projected electrostatic potential of the sample being imaged. However, once the electron exits the surface, it is focused by the electron optics onto the image plane of the objective lens. The wave function in the image plane is just the convolution of the exit wave and the point spread function of the optical system:

$$\psi_{image}(\mathbf{r}) = \psi_{exit}(\mathbf{r}) \otimes p(\mathbf{r}). \quad (6.13)$$

Taking the FT of both sides of Equation (6.13) gives us,

$$\Psi_{image}(\mathbf{r}^*) = \Psi_{exit}(\mathbf{r}^*) P(\mathbf{r}^*) \quad (6.14)$$

where $\Psi_{exit}(\mathbf{r}^*)$ and $\Psi_{image}(\mathbf{r}^*)$ are the FTs of the electron wave at the exit surface and imaging plane, respectively, and $P(\mathbf{r}^*)$ is the so called contrast transfer function

(CTF). The FT of the exit wave function is

$$\Psi_{\text{exit}}(\mathbf{r}^*) = \delta(\mathbf{r}^*) - i\sigma\Phi(\mathbf{r}^*) \quad (6.15)$$

where $\Phi(\mathbf{r}^*)$ is the FT of the projected potential, and $\delta(\mathbf{r}^*)$ is a delta function representing the transmitted beam. Combining the results from Equations (6.14) and (6.15), we get an equation relating the projected electrostatic potential to the electron wave function at the image plane:

$$\Psi_{\text{image}}(\mathbf{r}^*) = [\delta(\mathbf{r}^*) - i\sigma\Phi(\mathbf{r}^*)] P(\mathbf{r}^*) \quad (6.16)$$

In real space then, we have:

$$\psi_{\text{image}}(\mathbf{r}) = FT^{-1} \{[\delta(\mathbf{r}^*) - i\sigma\Phi(\mathbf{r}^*)] P(\mathbf{r}^*)\} \quad (6.17)$$

and the image intensity distribution is given by

$$I(\mathbf{r}) = (\psi_{\text{image}}(\mathbf{r})) \cdot (\psi_{\text{image}}(\mathbf{r}))^* \quad (6.18)$$

where $(\psi_{\text{image}}(\mathbf{r}))^*$ is the complex conjugate of $\psi_{\text{image}}(\mathbf{r})$.

Finally, it can be shown, [34], that the projected potential of the crystal is related to the FT of the HRTEM image as follows:

$$\varphi_z(x, y) = \frac{1}{2\sigma} \sum_h \sum_k \left\{ \frac{I(h, k)}{T(h, k)} \exp[-2\pi i(\mathbf{r}^* \bullet \mathbf{r})] \right\}. \quad (6.19)$$

Here, $T(\mathbf{r}^*)$ is related to the CTF,

$$T(\mathbf{r}^*) = P(\mathbf{r}^*) [2 \sin \chi(\mathbf{r}^*) \exp(-i\chi(\mathbf{r}^*))] \quad (6.20)$$

and

$$\chi(\mathbf{r}^*) = \pi \Delta f \lambda \|\mathbf{r}^*\|^2 + \frac{1}{2} \pi C_s \lambda^3 \|\mathbf{r}^*\|^4 \quad (6.21)$$

where Δf is the defocus value of the objective lens at the time of the image, and C_s is the coefficient of spherical aberration. Near the Scherzer defocus [45], $\Delta f = -\sqrt{\frac{4}{3} C_s \lambda}$, we can reduce Equation (6.19) further:

$$\varphi_z(x, y) \approx -\frac{1}{2\sigma} \sum_h \sum_k I(h, k) \exp[-2\pi i(\mathbf{r}^* \bullet \mathbf{r})] \quad (6.22)$$

or

$$\varphi_z(x, y) \approx -\frac{I(x, y)}{2\sigma} \quad (6.23)$$

So near Scherzer defocus, the projected potential $\varphi_z(x, y)$ is proportional to the image intensity $I(h, k)$, and correcting Fourier coefficient phases from the image is equivalent to solving for the structure factors of the crystal.

Lastly, it is important to realize that in TEM, the user is not limited to the information in a single image. For instance, sample misalignment and other 3D information can be determined by taking projections along different crystal axes or by examining diffraction patterns.

6.3 Imaging in STM

Unlike HRTEM images, where the contrast can be related to the projected electrostatic potential of a 3D crystal, the contrast mechanisms in SPM are related to tip-surface interactions between the microscope and sample. For instance, in STM, an atomically sharp tip (the ideal case) is brought close enough to the sample surface that the tip and sample's wave functions overlap. When a bias voltage is then applied, quantum tunneling occurs, from an occupied state of the sample to an unoccupied state of the tip, or vice versa depending on bias voltage [46].

Two standard modes of operation in STM are constant current and constant height mode. In constant height mode, the tip is rastered across the sample at a constant height, and changes in the tunneling current (which depends exponentially on the tip-surface distance) provides contrast in the image. In constant current mode, a feedback mechanism adjusts the height piezoelectrically such that the tunneling current remains constant and the tip height follows a contour of constant local density of states. Thus contrast can be related to the topography of the sample [47, 48]. A cartoon illustrating a typical STM and the interaction of the tip with the surface is shown in Figure 6.1.

FIGURE 6.1: Example of a typical STM operating in constant current mode. A (typically) tungsten tip is scanned across a sample in x and y while tunneling occurs at a constant rate (constant current) from occupied states in the sample to unoccupied states in the tip. A feedback mechanism controls a piezo which moves the tip in the z-direction such that a surface of constant local density of states is traced out by tip height variations.

As mentioned previously, most of the CIP procedures used for 2D crystals are valid for STM. If such an instrument is used to image the surface features of some regular 2D periodic array, one obtains a single 2D periodic image, as is the case for HRTEM. Any such real STM image may also be modeled by one of the 17 crystallographic plane symmetry groups. The difference is that in this case, the symmetry groups are not modeling a projected potential, but the actual symmetry of a 2D array. Additionally, we do not have to worry about sample thickness, optical distortion or other factors which might affect the dependence of image Fourier coefficients on the projected electrostatic potential. For STM (and SPM), we can safely assume that

the FT coefficients of an experimental image correspond directly to the local density of states in the image (or some other related surface feature).

Unfortunately, in applications of CIP to SPM, the user often has limited prior knowledge of the 2D plane symmetry that should be present, and a scanning probe microscopist may not have the same level of crystallographic intuition as a typical CIP user in the electron crystallography community. On top of that, some of the additional tools available in TEM, such as collecting diffraction patterns or imaging along other axes etc., are simply not possible. All of this makes the crucial CIP step of determining which plane symmetry to enforce more difficult.

7 Determining Plane Symmetry

7.1 Figures of Merit

For CIP to be useful, the manipulation of Fourier coefficients must be done in a very deliberate manner. This means that the user has to make some sort of determination about which plane symmetry group the experimental image is most closely modeled by. This symmetry determination is what differentiates CIP from similar methods such as simple translational averaging. Indeed, according to the developers of the widely used CIP software package CRISP, “*The symmetry determination part is the most specialized crystallographic part of CIP*” [49]. Of course, this issue of symmetry discrimination is not a new one, and a variety of techniques can be employed [33, 50].

There are several ‘figures of merit’ typically used by CIP software to judge which plane symmetry group best models the experimental image. These are (1) R-values on the Fourier coefficient magnitudes (in %), (2) ratios of the amplitude sum of plane group forbidden reflections to allowed reflections (‘extinction ratios’), and (3) the phase residuals (in $^{\circ}$), which were used to determine the phase origin in Section 5.2.2 [34]34].

7.1.1 FT Magnitude R-Values

The R-values for the FT magnitudes are simply

$$R_{\text{sym}} = \frac{\sum_h \sum_k ||F_{\text{obs}}(h k)| - |F_{\text{sym}}(h k)||}{\sum_h \sum_k |F_{\text{sym}}(h k)|}. \quad (7.1)$$

where $|F_{\text{obs}}(h k)|$ and $|F_{\text{sym}}(h k)|$ are the observed and symmetrized magnitude of the Fourier coefficient at (h, k) , respectively. This value quantifies how much the FT magnitudes in an experimental image deviate from a symmetrized image. Plane symmetry groups belonging to the same Bravais lattice or crystal class will usually have similar R_{sym} values.

7.1.2 Extinction Ratios

The extinction ratios A_0/A_e are mostly useful for determining if a centered lattice is present or not. Centered cells (and glide lines or screw axes) introduce restrictions on possible Fourier coefficients. In electron diffraction patterns, such forbidden peaks can be present if dynamical diffraction (i.e. non kinematical diffraction) occurs. This happens if the sample thickness is greater than the so called ‘extinction distance’. The reason behind this is that under dynamical diffraction conditions, electrons can be scattered multiple times traveling through the thicker sample, resulting in intensity where kinematical scattering theory predicts completely destructive interference of the electron waves.

For a given group, the ‘extinction ratio’ is just the sum of the magnitudes for all such

forbidden Fourier coefficients, divided by the sum of the magnitudes for all of the allowed FT coefficients. A large extinction ratio for a centered group in CIP would indicate that a lot of the supposed forbidden coefficients are present, and hence that group is not a very good model for the experimental image.

7.1.3 Phase Residuals

The phase residuals are the most important figure of merit for quantifying deviations of an experimental image from a symmetrized one. The phase residual for a particular plane symmetry group is defined as,

$$\phi_{res} = \frac{\sum_h \sum_k |F_{obs}(h k)| |\phi_{obs}(h k) - \phi_{sym}(h k)|}{\sum_h \sum_k |F_{obs}(h k)|} \quad (7.2)$$

where $|F_{obs}(h k)|$ is the observed magnitude of the Fourier coefficient at (h, k) , and $\phi_{obs}(h k)$ and $\phi_{sym}(h k)$ are the observed and symmetrized phases, respectively.

Notice that the phases for index (h, k) are weighted by the corresponding magnitudes in the calculation of the phase residual. The reasoning behind this is that for a sinusoidal signal with small amplitude, noise can make it difficult to determine phase, as shown in Figure 7.1. So the phases of high magnitude coefficients are more reliable. To see it another way, notice that the vector difference between an observed and symmetrized Fourier coefficient, plotted as phasors, will be greater for large magnitude coefficients, even if the phase difference $\Delta\phi$ is the same, as in Figure 7.2.

It is typically up to the user to interpret these residuals and determine which plane

FIGURE 7.1: Difficulty in distinguishing a signal from noise (and hence difficulty in determining its phase) is increased for low amplitude signals. Phase measurements from high amplitude signals are more reliable and should be weighted more heavily.

symmetry group should be enforced. In general, the group with the lowest phase residual is chosen. There is often an implicit reliance on the possession of prior knowledge or crystallographic intuition when making these decisions, and in some cases an explicit reliance on rules of thumb.

FIGURE 7.2: The vector difference between Fourier coefficients is larger for the same phase change if the magnitudes of the coefficients are bigger. Here, ϕ_1 , ϕ_2 and $\Delta\phi$ are the same for both phasor diagrams, but $B > A$.

7.2 Examples from Other CIP Software

In this section we illustrate with screenshots the use of phase residuals for symmetry determination in several popular CIP computer programs. In Figure 7.3, we see a screen capture of the software VEC the residual map (equivalent to our phase origin map), as well as the phase residual value (circled) for group $p4mm$ [37]. If one has no prior knowledge of the 2D symmetry present, symmetry determination can be tedious as the user cannot directly compare phase residuals without selecting each group one by one.

Figure 7.4 shows the software EDM, with all of the calculated residuals displayed on the left (circled) [36]. In this case, residuals were calculated for only the hexagonal groups due to the shape of the experimental unit cell. The manual for this software

FIGURE 7.3: Screenshot of CIP software VEC [37]. The phase residual for group $p4mm$ is circled. Users must click on each group individually to compare residuals for each group. This is generally not a problem as users of this software usually have some idea about which plane symmetry should be enforced.

also makes it clear that the phase residuals alone may not be adequate:

“Caveat: the phase residuals will always be smallest for $P1$, which does not mean that it is right! Which symmetry to use is a choice that you have to make, there are no rules which are always true.”

In Figure 7.5, we have the program CRISP, which shows on the left panel the phase residuals (circled), as well as the other two figures of merit mentioned in Section

FIGURE 7.4: Screenshot of the CIP software EDM [36]. In this case, all of the calculated phase residuals are displayed together (circled), making it less tedious to compare values for different possible plane symmetry groups. Notice that for a given Bravais lattice type (here a hexagonal lattice), subgroups will always have a smaller phase residual than their supergroups.

7.1. Similar to EDM, the CRISP programmers leave us with a rule of thumb for interpreting phase residuals:

“The rule is that the highest possible symmetry should be chosen if you are in doubt. If you can collect higher quality images, you may be able to rule out the more symmetric plane groups.”

Finally, a screenshot of our own CIP software is shown in Figure 7.6, with phase

FIGURE 7.5: Screenshot of CIP software CRISP [35]. Here all three figures of merit discussed above are displayed on the left panel (phase residuals circled). Additionally, it appears as if 21 (instead of 17) groups are shown, because different orientations of mirror and glide lines are tested for several groups (indicated by the second column from the left). The far right panel is a phase origin map, similar to the one from our software shown earlier, Figure 5.2.

residuals circled. Notice that our display is very similar to CRISP, with all three figures of merit shown.

FIGURE 7.6: A screenshot of our software T4SC processing a simulated plane symmetry group pattern. All three figures of merit are displayed on the left panel, with phase residuals highlighted. The interface of this module of the software is similar to that of CRISP.

8 Geometric Akaike Information Criterion

8.1 Why is a Statistical Criterion Necessary?

Now we point out that the 17 plane symmetry groups are non-disjoint. That is to say, there are inclusion relations in the form of type **I** *translationengleiche* and type **IIa** *klassengleiche* non-isomorphic subgroup-supergroup relationships, where a supergroup contains all of the elements of a subgroup plus at least one additional unshared element, as described in the ITC Vol. A [14]. The type **I** inclusion relations are shown in Figure 8.1.

FIGURE 8.1: Type **I** *translationengleiche* inclusion relations between the 17 plane symmetry groups. A group lower on the diagram is a subgroup of (included in) a group which it is connected to higher on the diagram. Color (grayscale) indicates Bravais lattice type, and the multiplicity of the general position per lattice point is indicated by height in the diagram.

The fact that CIP users must rely on rules of thumb for phase residuals to determine symmetry is a direct consequence of this non-disjointness. Similar problems arise frequently when comparing classes of models with inclusion relations. This is because the model with the fewest constraints (least symmetric model) will always be favored by any ‘distance measure’ (how much experimental data differs from various models), because *“the discrepancy between the data and the model become larger as the model is more restricted”* [51].

For example, consider the following distance measure, d , between any two arbitrary shapes P and Q , made up of n points, $\{P_i\}_{i=1}^n$ and $\{Q_i\}_{i=1}^n$, respectively:

$$d(P, Q) = \frac{1}{n} \sum_{i=1}^n \|P_i - Q_i\|^2 \quad (8.1)$$

In [52], a ‘continuous symmetry measure’ was derived between a shape with n points $\{P_i\}_{i=1}^n$ and its so called ‘symmetry transform’, P' , with points $\{P'_i\}_{i=1}^n$. The symmetry transform is an ideal shape with n -fold rotation symmetry about its centroid. A similar transform is defined to take a shape with $q \cdot n$ points $\{P_i\}_{i=1}^{qn}$ to an n -fold symmetric shape. This continuous symmetry measure mentioned above is defined as the distance from Equation (8.1), between a shape P and its symmetry transform P' , $d(P, P')$.

It can be shown that of all possible n -fold symmetric shapes, the symmetry transform P' gives the minimum distance $d(P, P')$ [52]. A continuous symmetry measure such as this allows us to quantify deviations of an observed shape from one with ideal

symmetry. Nevertheless, if we want to use this symmetry measure to choose a model for an observed, non-symmetric shape, we can run into the same problem of non-disjointness. For instance, 3-fold symmetry is included in 6-fold symmetry, and so the distance d between the observed shape and a symmetric one will always be less for the 3-fold shape than 6-fold.

8.2 Defining the Geometric AIC

In the robotics and computer vision communities, model selection involving non-disjoint classes of models often employs geometric AICs [51, 53, 54]. The use of the geometric AIC for model selection relies on a deviation from traditional statistical inference. Typically, statistical inference involves formulating some type of structure or statistical model which describes some phenomena. Such a model contains both deterministic and indeterministic (i.e. noise) parameters. Any deviations from the statistical model are defined as noise from various unknown sources. The noise is an inherent part of the statistical model itself.

For geometric model selection, we assume that the noise is a completely separate entity from the model in question, regardless of the model being used. In the cases we are most interested in, the noise could be generated from a blunt STM tip, image processing algorithm, limitations of a CCD camera when digitizing HRTEM images, etc., which are independent of the symmetry model being imposed on an image. For this type of geometric inference, the noise level, σ , is taken as the asymptotic variable. This is in contrast to usual statistical inference in which the asymptotic variable is the

number of observations n . The following thought experiment as given by Kanatani illustrates the equivalence of the two scenarios [55]:

“Suppose we observe an image many times. In reality, the result is always the same as long as the image and image processing algorithms involved are the same. It is, therefore, impossible to observe a different occurrence of the ‘noise’, by which we mean the inaccuracy due to the limited resolution and imperfection of the processing algorithms. In this sense, the number n of observations is always 1. However, if we hypothetically imagine that noise occurrence changes independently each time we observe the same image, then we could obtain more accurate data by taking the average of the n observations. This means that increasing the number n of hypothetical observations is equivalent to effectively reducing the noise level σ ” .

When determining plane symmetry in CIP for a STM image of a regular 2D periodic array of surface features, for instance, the 16 higher symmetric plane symmetry groups are the models we are discriminating between. Because all of our models are derived by enforcing symmetry on one single experimental image, we can assume the same type of Gaussian noise is present, regardless of the model chosen. Geometric model selection in this case is then equivalent to making an inference about the symmetry of the object being imaged, if the independent Gaussian noise σ had been effectively

reduced to zero. This is similar to making a statistical inference about a population's age distribution, for instance, if the population size n were to approach infinity.

Consider a set of data with N degrees of freedom. A geometric model S , defined by L constraint equations, is then a sub-manifold in the N -dimensional data space. For a linear subspace of a finite dimensional vector space, the co-dimension is related to the dimension of the subspace as follows:

$$\text{codim}(\text{subspace}) = \dim(\text{space}) - \dim(\text{subspace}) \quad (8.2)$$

If this sub-manifold S is a linear subspace of the data space, with dimension $N - L$, then the co-dimension of the sub-manifold is simply L . Optimally enforcing the model S on the data is equivalent to orthogonally projecting the data in N -dimensional space, $\{x_i\}$, onto the sub-manifold S to create constrained data, $\{y_i\}$, as shown in Figure 8.2.

The residual for the model S is just the sum of squared differences between the data points and their corresponding orthogonal projections:

$$\hat{J} = \sum_i \|x_i - y_i\|^2 \quad (8.3)$$

Assume a model S with dimension d , n degrees of freedom (the degrees of freedom of the vector which parameterizes the constraints) and independent Gaussian noise

N-dimensional space

FIGURE 8.2: Optimally enforcing a model S upon data $\{x_i\}$ with N degrees of freedom is equivalent to orthogonally projecting the data onto a sub-manifold in the N -dimensional data space.

of mean zero, σ . The geometric AIC in such a case is defined as follows [56]:

$$AIC(S) = \hat{J} + 2(dN + n)\sigma^2 \quad (8.4)$$

To compare two models with an inclusion relation, we can estimate the noise according to the weaker of the two models (model with fewest constraints). For instance, suppose we have a model S_1 of dimension d_1 , co-dimension r_1 , and n_1 degrees of freedom. Similarly, model S_2 has dimension d_2 , co-dimension r_2 and n_2 degrees of freedom. If S_2 is a stronger model than S_1 (i.e. obtained by imposing some additional constraint(s) on model S_1), it can be shown, [56], that in the first order, the following

is an unbiased estimator of the squared noise:

$$\hat{\sigma}^2 = \frac{\hat{J}_2}{r_2 N - n_2} \quad (8.5)$$

The favored model is determined by a comparison of their geometric AIC values rather than their residuals alone. For a more constrained model S_2 to be favored over a weaker model S_1 , the following inequality must be satisfied:

$$AIC(S_2) < AIC(S_1) \quad (8.6)$$

Substituting from Equation (8.4),

$$\hat{J}_2 + 2(d_2 N + n_2) \sigma^2 < \hat{J}_1 + 2(d_1 N + n_1) \sigma^2 \quad (8.7)$$

and taking the ratio of the two residuals gives us,

$$\frac{\hat{J}_2}{\hat{J}_1} < 1 + \frac{[2(d_1 - d_2) N + 2(n_1 - n_2)] \sigma^2}{\hat{J}_1} \quad (8.8)$$

From here, we simply substitute in our estimator for the squared noise from Equation (8.5):

$$\frac{\hat{J}_2}{\hat{J}_1} < 1 + \frac{[2(d_1 - d_2) N + 2(n_1 - n_2)]}{\hat{J}_1} \frac{\hat{J}_1}{r_1 N - n_1} \quad (8.9)$$

Finally, we find that a more constrained model will be favored over a less constrained model so long as the following inequality is satisfied:

$$\frac{\hat{J}_2}{\hat{J}_1} < 1 + \frac{2(d_1 - d_2)N + 2(n_1 - n_2)}{r_1N - n_1} \quad (8.10)$$

8.3 Geometric AIC Applicable to Model Selection in CIP

8.3.1 Inclusion Relations of Special Quadrilaterals

As another example, the geometric AIC has been used to classify mouse drawn (i.e. line tool in paint program) quadrilaterals as one of the quadrilaterals with at least the symmetry of a trapezoid (trapezium outside of North America) [57]. In the Euclidian plane, any such quadrilateral is subject to one or more constraints. In particular, the vectors defining the vertices of these shapes (trapezoid, parallelogram, rectangle, square) are subject to certain constraints. If the 4 vectors are defined as shown in Figure 8.3, then we have 4 specific types of constraints for the quadrilaterals listed above, all involving cross products or dot products (5 constraints if we include the special case of a rhombus with an interior angle of 120° , which is of importance to our particular application). These constraints are also shown in Figure 8.3.

The inclusion relations that make these classes of quadrilaterals non-disjoint should be familiar to most. Mathematically, the set of all squares is a subset of (included in) the set of all rectangles, and the set of all rectangles is a subset of (included in) the set of all parallelograms, etc. These special quadrilaterals are illustrated in the

- $$\begin{aligned}
 & \left. \begin{aligned} 1] (\vec{x}_2 - \vec{x}_1) \times (\vec{x}_4 - \vec{x}_3) &= 0 \\ 2] (\vec{x}_3 - \vec{x}_1) \times (\vec{x}_4 - \vec{x}_2) &= 0 \end{aligned} \right\} \text{Opposite sides are parallel} \\
 & \left. \begin{aligned} 3] (\vec{x}_3 - \vec{x}_1) \bullet (\vec{x}_4 - \vec{x}_3) &= 0 \end{aligned} \right\} \text{Adjacent sides are orthogonal} \\
 & 4] (\vec{x}_4 - \vec{x}_1) \bullet (\vec{x}_3 - \vec{x}_2) = 0 \left. \vphantom{\begin{aligned} 3] (\vec{x}_3 - \vec{x}_1) \bullet (\vec{x}_4 - \vec{x}_3) = 0 \end{aligned}} \right\} \text{Diagonals are orthogonal} \\
 & 5] (\vec{x}_3 - \vec{x}_1) \bullet (\vec{x}_4 - \vec{x}_3) = \pm \frac{1}{2} |\vec{x}_3 - \vec{x}_1| \cdot |\vec{x}_4 - \vec{x}_3| \left. \vphantom{\begin{aligned} 3] (\vec{x}_3 - \vec{x}_1) \bullet (\vec{x}_4 - \vec{x}_3) = 0 \end{aligned}} \right\} \text{Angle is } 60^\circ \text{ or } 120^\circ
 \end{aligned}$$

FIGURE 8.3: Geometric constraints on the vertices of quadrilateral with at least the symmetry of a trapezoid (trapezium outside of North America) in the Cartesian plane. A square, for instance, is subject to constraints 1 – 4. A rectangle is only subject to a subset of the square’s constraints (1, 2, 3). This constitutes an inclusion relation. The fifth constraint is included to distinguish between a rhombus with or without an interior angle of 120° .

inclusion relation diagram of Figure 8.4, along with the particular constraints (from Figure 8.3) which apply to each shape.

It is also possible to construct an equivalent inclusion relation diagram in crystallographic terms. The holohedral crystallographic point groups are shown in Chapter 2 (Table 2.3). A plane symmetry group containing a holohedral point symmetry is referred to as the ‘holohedral plane symmetry group’ for a crystal family, and is the plane symmetry group of the Bravais lattice. We can create an inclusion relation diagram for these holohedral plane symmetry groups, where the constraints take the form of non-translational symmetry operations which are generators for the group. This is done in Figure 8.5. The ITC descriptions of these holohedral plane symmetry groups, with the non-translational group generators highlighted, are given in Appendix B.

It should now be evident to the reader that the special quadrilaterals discussed above which are subject to two or more constraints on their vertices (Figure 8.4) correspond to the unit cell shapes of four of the five 2D Bravais lattices, Figure 8.6. For the rectangular centered Bravais lattice, *oc*, a primitive unit cell (not the conventional unit cell for this Bravais lattice) can be used, which corresponds to the shape of a rhombus with no interior angles equal to 120° . These shapes can be defined in terms of either the geometric constraints on their vertices (Figures 8.3 and 8.4), or the non-translating generators of the plane symmetry holohedries for the corresponding lattice (Figure 8.5). In other words, a classification scheme similar to the one derived

FIGURE 8.4: Inclusion relation diagram showing hierarchy of quadrilaterals. The number of constraints, as well as the particular constraints (from Figure 8.3) for each shape are shown. Arrows between shapes indicate that the constraints of the bottom shape are a subset of (included in) the constraints of the top shape.

FIGURE 8.5: Holohedral plane group inclusion relation diagram. Plane symmetry groups which contain a holohedral point group are listed, along with the Bravais lattice type. The non-translational group generator operators (and their position within the unit cell) are given according to the convention used in the ITC. It should be noted that the ITC only uses the centered cell for group $c2mm$, so the constraints (generators) are the same as for a rectangular centered lattice ($p2mm$). In analogy with Figure 8.4, we are interested in the primitive unit cell for $c2mm$, for which the ITC has no convention.

in reference [57] for model selection of these special quadrilaterals, can also be applied to unambiguously determine the most likely 2D Bravais lattice in an experimental image.

FIGURE 8.6: (a-d) Unit cell shapes corresponding to the four primitive 2D Bravais lattices. (e) Unit cell shape for the unconventional primitive unit cell of the centered 2D Bravais lattice. These all correspond to the quadrilaterals with 2 or more constraints on their vertices (Figure 8.4)

8.3.2 Deriving the Criterion

As a distance measure, we define a residual J , which is the sum of squared distances between the vertices of an experimental shape and one of the model shapes. Our calculation of this residual for a particular model is given in Appendix A.

For an arbitrary polygon defined by N vertices x_i , each with 2 degrees of freedom, we can define a point in a $2N$ -dimensional space by the direct sum $\oplus_{i=0}^{N-1} x_i$. If a model S has L constraint equations (as defined in Figures 8.3 and 8.4 for instance), then the points x'_i for the model S are the orthogonal projection of $\oplus_{i=0}^{N-1} x_i$ onto a manifold of dimension $d = 2N - L$ and co-dimension $r = L$.

A quadrilateral ($N = 4$) in the Cartesian plane, for instance, requires that the position of all 4 vertices be known to uniquely define its shape. Since each vertex has two coordinates, the shape has $2N = 8$ degrees of freedom, and can be described by a single point in an 8-dimensional space. A square, on the other hand, requires the coordinates of only two vertices to completely describe its shape, giving it a degree of freedom of 4. This is because its vertices are subject to $L = 4$ constraints, meaning it is defined as a point on a 4-dimensional ($2N - L = 4$) sub-manifold of the original 2N-dimensional data space.

Referring to Equation (8.10), when comparing the residuals of two models, a more symmetric model S' will be statistically favored over a less symmetric model S if the following condition is satisfied:

$$\frac{J'}{J} < 1 + \frac{2[(2N - L) - (2N - L')]N + 2(L - L')}{LN - L} \quad (8.11)$$

where J' and J are the residuals, and L' and L are the numbers of constraints for models S' and S , respectively. After combining terms and factoring out the L' and

L , we get,

$$\frac{J'}{J} < \frac{2L'(N-1) - L(N-1)}{L(N-1)} \quad (8.12)$$

Finally we see that the factors involving the number of vertices, N , cancel out, and the ratio depends only on the numbers of constraints for each model:

$$\frac{J'}{J} < \frac{2L' - L}{L} \quad (8.13)$$

This is exactly equation (3) from reference [57]. We now have a definitive point at which we can classify a figure unambiguously as one of the special quadrilaterals of Figure 8.4. If Equation (8.13) holds, the more symmetric model is favored. If the inequality is not satisfied, the less constrained model is favored.

As an example, we see from Figure 8.4 that a square has 4 constraints, while a rectangle has only 3. Then according to Equation (8.13), the constraints of a square are statistically favored over those of a rectangle as the model for an experimental shape so long as the residual J' for the square model is at most $5/3$ as large as J , the residual for the rectangular model. So a square can be chosen even if it has a larger residual. We emphasize again that there is no need for a rule of thumb because there is no ambiguity; we have a square or a rectangle depending on whether the inequality (Equation (8.13)) is satisfied or not, respectively.

8.3.3 Determining a 2D Bravais Lattice

When the Fourier transform is indexed, as described in Section 5.2.1, the direct space lattice parameters (which define the shape of the unit cell) are determined. However, the parameters from this initial indexing only correspond to the oblique lattice and the translational averaged unit cell (plane group $p1$) of the experimental image. The additional lattice parameters are generated when one of the plane symmetry groups is enforced on the Fourier coefficients. As described in Section 5.2.2, a plane symmetry group is enforced by averaging symmetry related coefficients. As a result, some peaks in the amplitude map can become much smaller, and entirely new peaks can appear. These changes in the amplitude map naturally affect the lattice indexing, resulting in a new set of lattice parameters. The closer the experimental image is to one of the 16 higher symmetric plane groups, the less impact the symmetrization will have on the symmetrized Fourier coefficients and lattice parameters of the other 4 Bravais lattices.

In Figure 5.1 above, for example, the oblique (experimental) lattice parameters already appear square because a simulated image with $p2mm$ symmetry was used. Thus, enforcing the symmetry elements in $p2mm$ would leave the lattice parameters unchanged. Although the CIP procedure creates a symmetrized image for all 17 plane symmetry groups, there are only 5 unique sets of lattice parameters corresponding to the 5 Bravais lattice types. Thus, multiple groups which are compatible with the same Bravais lattice will have the same lattice parameters, though the symmetrized

images themselves can still differ.

Consequently, we can determine which Bravais lattice is most likely present in the image (if the effect of the less than perfect imaging process (e.g. noise) were removed) by classifying the unit cell shape as one of the special quadrilaterals of Figure 8.4. A Bravais lattice is compatible with (at most) 5 plane symmetry groups (Figure 8.1). So we have effectively reduced the problem from choosing between 17 plane symmetry groups to at most 5 plane symmetry groups during the CIP procedure.

It is important to emphasize that the criterion in Equation (8.13) only applies between non-disjoint shapes. For a rectangle and rhombus, for instance, we cannot use the geometric AIC because there is no inclusion relation between the constraints of the two shapes (they are not connected directly on the diagram in Figure 8.4). However, in certain circumstances the residuals for the two shapes (models) can be compared indirectly using simple logic. For instance, if the criterion in Equation (8.13) tells us that a rectangle is statistically favored over a parallelogram, and a parallelogram is favored over a rhombus, then it is logical to say that a rectangle is statistically favored over a rhombus, even though we could not compare them using the geometric AIC directly. If instead, we found that both a rhombus and a rectangle are statistically favored over a parallelogram, we are at an impasse and can make no assumption about which model is a better fit based on the geometric AIC alone. Examples of the logical results (favored Bravais lattice/lattices) of applying the geometric AIC criterion to compare various unit cell shapes are given in Figure 8.7.

$J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} > \left(\frac{5}{3}\right) J_{\text{rhombus}}$	square
$J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}}$	hexagonal
$J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} > \left(\frac{5}{3}\right) J_{\text{rhombus}}$	centered
$J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} > \left(\frac{5}{3}\right) J_{\text{rhombus}}$	rectangular
$J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}}$	square or hexagonal
$J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}}$	hexagonal or rectangular
$J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} \leq \left(\frac{5}{3}\right) J_{\text{rhombus}}$	hexagonal or rectangular
$J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rectangle}} ; J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rhombus}} ; J_{\text{hexagonal}} > \left(\frac{5}{3}\right) J_{\text{rhombus}}$	rectangular or centered
$J_{\text{rectangle}} > 2J_{\text{parallelogram}} ; J_{\text{rhombus}} > 2J_{\text{parallelogram}} ; J_{\text{parallelogram}} \leq 3J_{\text{trapezoid}}$	oblique

FIGURE 8.7: Some examples of how we can determine which 2D Bravais lattice is favored in an experimental image even when the unit cell shapes are disjoint. Additional scenarios besides those listed are possible.

9 Some Examples

9.1 STM Image of Cobalt Phthalocyanine on Au (111)

Now we look at an STM image of cobalt (II) phthalocyanine (CoPc) on an Au (111) substrate taken at Washington State University, Figure 9.1 [58]. A monolayer of CoPc was formed by exposing the gold substrate to 10^{-6} Molar ethanolic $\text{KCoPc}(\text{CN})_2$ for ten minutes, washing it with ethanol, and finally annealing it at 110°C . The image was taken with a PtIr tip under UHV with a tunneling current of 100 pA and a bias voltage of +0.75 V.

The figures of merit after CIP analysis of this image are shown in Table 9.1. For brevity, only the most likely group (based on their figures of merit) for each Bravais lattice type are shown here for comparison. One might have some trouble deciding which plane symmetry group to enforce based on these residuals. Group $p4$ has low phase residuals and R-values, but both cm and $p2$ have smaller phase residuals, which are usually weighed more heavily. Group cm has a rather large extinction ratio, indicating that a centered cell is not the best choice. $p2$ will always have a smaller phase residual than $p4$, so we cannot make a choice based on that alone.

Using the geometric AIC (Equation (8.13)), along with the residual (far right column in Table 9.1), we determine that the constraints of a square lattice are favored over those for an oblique one, and hence we choose group $p4$. The insets in Figure 9.1 are the symmetry enforced $p2$ and $p4$ images, along with the $p4$ enforced contour map.

FIGURE 9.1: STM image of CoPc on an Au (111) substrate taken at Washington State University [58]. A monolayer of CoPc was formed by exposing the gold substrate to 10^{-6} Molar ethanolic $\text{KCoPc}(\text{CN})_2$ for ten minutes, washing it with ethanol, and finally annealing it at 110°C . The image was taken with a PtIr tip under UHV with a tunneling current of 100 pA and a bias voltage of +0.75 V. (insets) $p2$ and $p4$ enforced images. (b) $p4$ contour plot with unit cell outlined (in red), created with software CRISP [35].

TABLE 9.1: Figures of Merit for CIP Symmetry Determination of CoPc on Au (111)

Group	R_{sym} (%)	ϕ_{res} (°)	A_0/A_e	Residual J
$p2$	-	12.3	-	1.00
pm	23.8	21.1	-	1.01
cm	19.8	11.8	2.4	1.10
$p4$	12.3	13.0	-	1.15
$p3$	59.1	18.6	-	105.30

We see that the difference in the two figures is almost imperceptible. This normally indicates that the higher symmetry group is present in the image. Notice that the first 4 values of the residuals are very close, but obey the following relation:

$$J_{\text{square}} > J_{\text{rectangular}}/J_{\text{centered}} > J_{\text{oblique}}. \quad (9.1)$$

This illustrates the problem already discussed with models that have inclusion relations. Using distance measures alone, a lower symmetric group will always be favored over a more symmetric group related by an inclusion relation. Thus, even when the experimental image is very close to matching a higher symmetric model (as was the case here with the square lattice), the lower symmetric model is closer. Figure 9.2 is an illustration of the CoPC molecule.

9.2 STM Image of Nominal Cobalt Phthalocyanine on Ag (111)

In Figure 9.3, we have an STM image of nominal CoPc on an Ag (111) substrate, taken at the taken at the Chemnitz University of Technology at cryogenic temperatures (about 30 K), with a tunneling current of 150 pA and bias voltage of -1.0 volts [59].

FIGURE 9.2: Representation of a cobalt phthalocyanine molecule (formula $\text{C}_{32}\text{H}_{16}\text{CoN}_8$). There is a heavy cobalt atom in the center, and light hydrogen atoms on the outer edges of 4 carbon rings. Image adapted from: <http://www.org-chem.org/yuuki/mow/0502/phthalocyanin.html>

The figures of merit after CIP analysis of this image are shown in Table 9.2. Again, only the most likely group (based on their figures of merit) for each Bravais lattice type are shown here for comparison.

Groups $c2mm$ and $p2mm$ are likely candidates due to lower phase residuals and R-values. $c2mm$ has a moderate extinction ratio, but the very low phase residual makes it hard to dismiss. According to the residual and Equation (8.13), a square lattice is favored over the rectangular centered and rectangular primitive lattices, indicating

FIGURE 9.3: STM image of nominal CoPc on an Ag (111) substrate, taken at the taken at the Chemnitz University of Technology at cryogenic temperatures (about 30K), with a tunneling current of 150 pA and bias voltage of -1.0 volts. The region used for CIP analysis is circled.

TABLE 9.2: Figures of Merit for CIP Symmetry Determination of Nominal CoPc on Ag (111)

Group	R_{sym} (%)	ϕ_{res} ($^{\circ}$)	A_0/A_e	Residual J
$p2$	-	6.4	-	1.00
$p2mm$	27.3	6.4	-	1.76
$c2mm$	30.9	3.6	0.8	1.15
$p4mm$	35.5	7.2	-	1.85
$p3$	62.2	19.1	-	240.78

that plane symmetry group $p4mm$ best fits the image.

Figure 9.4 shows the contour plots and the symmetry enforced image for both $c2mm$ and $p4mm$. To the human eye, the $p4mm$ image looks much closer to Figure 9.3 than the $c2mm$ image does. The $p4mm$ image has two distinct repeating shapes, as did the experimental image, whereas in the $c2mm$ image does not.

9.3 STM Images of Tetraphenoxypthalocyanine on Graphite

Figures 9.5 and 9.7 show STM images of the same molecular array of tetraphenoxypthalocyanine (H_2PcPhO) on highly oriented pyrolytic graphite (HOPG), at two different magnifications([60] and personal communication 2011). Based on the CIP processing of approximately 90 molecules of the array (Figure 9.5), and utilizing the classical CIP residuals (Table 9.3), one would probably conclude that the plane symmetry group pg should be enforced. We see that two of the three classical figures of merit (most importantly the phase residual) slightly favor pg over cm . However, one might be reluctant to choose cm because there are only the rules of thumb, and no statistically sound basis for making this choice.

FIGURE 9.4: Contour plots created with CRISP [35] (top) and symmetry enforced images (bottom) for $c2mm$ (left) and $p4mm$ (right). The $p4mm$ enforced image as well as the density map are in close agreement with both the experimental image (Figure 9.2) and the shape of the CoPc molecule (Figure 9.3.)

FIGURE 9.5: STM image of approximately 90 molecules of H₂PcPhO on graphite. The circular region (blue in color version of this paper) was selected for FT and subsequent CIP analysis. Inset is a map of the FT magnitudes and a close up of the pixels around one of the peaks, with pixel intensity values included. For this many molecules, the peak is not as sharp as we would like, and we expect the figures of merit (Table 9.3) to be a little worse than those corresponding to the Figure 9.7 (Table 9.4).

TABLE 9.3: Symmetry Determination for Tetraphenoxypthalocyanine on Graphite (Based on CIP of Approximately 90 Molecules)

Group	R_{sym} (%)	ϕ_{res} (°)	A_0/A_e	Residual J
$p2$	-	24.6	-	1.00
pm	20.6	12.8	-	20.070
pg	21.1	10.0	0.6	
$p2mm$	20.6	28.7	-	
$p2mg$	21.1	25.3	0.6	
$p2gg$	21.8	23.7	0.5	
cm	19.8	10.9	0.8	1.002
$c2mm$	19.8	22.2	0.8	
$p4$	31.7	28.3	-	20.973
$p4mm$	33.8	31.4	-	
$p4gm$	32.7	26.1	0.5	
$p3$	80.5	10.6	-	9.166
$p3m1$	83.7	19.6	-	
$p31m$	83.7	19.6	-	
$p6$	80.5	27.4	-	
$p6mm$	83.7	32.7	-	

On the other hand, the residuals J , calculated for the different unit cell shapes corresponding to the possible Bravais lattices (steps in Appendix A), combined with the geometric AIC (Equation (8.13)), indicate that a rectangular centered lattice is statistically likely. According to the criterion in Equation (8.13), a rectangular centered lattice is favored over a rectangular lattice if the following conditions are met:

$$J_{\text{square}} \leq \left(\frac{5}{3}\right) J_{\text{rectangle}} \quad \text{and} \quad J_{\text{square}} > \left(\frac{5}{3}\right) J_{\text{rhombus}} \quad (9.2)$$

This is clearly true, so we can conclude that the plane symmetry present is at least cm (thus excluding pg).

Further evidence that the plane symmetry group is indeed cm is provided by the two contour plots of Figure 9.6. The pg contour plot shows two different average electron densities of states at the Fermi level for the same type of molecule; this is quite unreasonable. On the other hand, the cm contour plot shows only one such density of states, which possesses a mirror line through the molecules.

FIGURE 9.6: On the (left) we have a contour plot showing 1.5 unit cells of the pg enforced image, and on the (right) we have the same for the cm enforced image. The pg plot indicates two different average electron densities of states at the Fermi level for the same type of molecule, whereas the cm plot indicates only one average density of states. Contour plots created with CRISP software [35].

All of these conclusions are borne out in Figure 9.7 and Table 9.4, where our analyses were based on a larger section (approximately 450 molecules) of the same array. Since CIP is at its core an averaging technique, this constitutes a better set of data for CIP

analysis. This can also be seen by comparing the FT magnitudes (insets of Figures 9.5 and 9.7) for both experimental images. Much ‘cleaner’ peaks, with more precise peak positions can be seen in the latter case. This leads to less uncertainty in the positions of magnitude peaks in the FT, and thus more accuracy in the traditional figures of merit.

TABLE 9.4: Symmetry Determination for Tetraphenoxypthalocyanine on Graphite (Based on CIP of Approximately 450 Molecules)

Group	R_{sym} (%)	ϕ_{res} (°)	A_0/A_e	Residual J
$p2$	-	20.0	-	1.000
pm	13.3	11.2	-	8.119
pg	14.1	8.2	1.0	
$p2mm$	13.3	23.4	-	
$p2mg$	14.1	18.8	1.0	
$p2gg$	14.5	18.8	0.6	
cm	12.7	6.8	0.6	1.001
$c2mm$	12.7	15.1	0.6	
$p4$	21.4	21.3	-	8.157
$p4mm$	23.6	25.1	-	
$p4gm$	22.0	19.2	0.6	
$p3$	75.5	10.8	-	47.58
$p3m1$	79.7	15.1	-	
$p31m$	79.7	15.2	-	
$p6$	75.5	22.7	-	
$p6mm$	79.7	22.8	-	

In Table 9.4, we see that all three classical CIP figures of merit and our geometric AIC residual unambiguously identify cm as the most likely plane symmetry present in the experimental STM image. Thus, by determining the most likely Bravais lattice

FIGURE 9.7: STM image of approximately 450 molecules of H₂PcPhO on graphite. The circular region (blue in color version of this paper) was selected for FT and subsequent CIP analysis. Inset is a map of the FT magnitudes and a close up of the pixels around one of the peaks, with pixel intensity values included. Since CIP is essentially an averaging technique, we would expect better results with so many repeats of the molecule. Indeed, we see that the peak in the FT magnitude map is much ‘cleaner’ in this case, and as a result, the CIP figures of merit (Table 9.4) should be more accurate than was the case for Figure 9.5 and Table 9.3.

based on the geometric AIC, we found that the experimental image is best modeled by the plane symmetry group cm , and then reinforced this conclusion based on the traditional CIP residuals from a higher quality data set.

The fact that the cm symmetry appears to be present here indicates that the symmetric H_2PcPhO molecules have broken mirror symmetry. This could indicate that the molecules are not lying flat, but are tilted relative to the substrate due to the weak interaction of the graphite.

9.4 STM Image of Hexaazatriphenylene-hexacarbonitrile Molecules on Ag (111)

In Figure 9.8, we have an image of a monolayer of hexaazatriphenylenehexacarbonitrile (HATCN) on Ag (111) substrate, taken with a STM at Humboldt University in Berlin [61]. The image was taken at room temperature under UHV with a tunneling current of 0.3 nA and a bias voltage of -1.0 volts. Figures of merit from the CIP analysis of the circular region of Figure 9.8 are shown in Table 9.5.

In this case, we see that the traditional CIP residuals favor the plane symmetry groups corresponding to a hexagonal Bravais lattice. The residuals J are in agreement with this, in that the geometric AIC tells us that the constraints of a rhombus with an interior angle of 120° is statistically favored over those of an ordinary rhombus, which in turn is statistically favored over the constraints of a square.

Unfortunately, there are 5 plane symmetry groups which are compatible with a hexagonal Bravais lattice: $p3$, $p3m1$, $p31m$, $p6$ and $p6mm$. At this stage, the user must still rely on traditional CIP residuals to determine which of these 5 groups best fits

FIGURE 9.8: STM image of hexaazatriphenylenehexacarbonitrile (HATCN) on Ag (111) substrate. Image taken at room temperature under UHV with a tunneling current of 0.3 nA and a bias voltage of -1.0 volts [61]. The circular region (blue in color version of this paper) was selected for FT and subsequent CIP analysis.

Selected CIP figures of merit from this analysis are shown in Table 9.5.

TABLE 9.5: Symmetry Determination for Hexaazatriph-
enylenehexacarbonitrile on Ag (111)

Group	R_{sym} (%)	ϕ_{res} ($^{\circ}$)	A_0/A_e	Residual J
$p2$	-	12.9	-	1.00
pm	33.2	12.1	-	218.01
pg	41.4	14.1	2.1	
$p2mm$	33.2	18.7	-	
$p2mg$	41.4	19.4	2.1	
$p2gg$	57.3	33.7	2.4	
cm	60.2	9.2	1.1	1.05
$c2mm$	60.2	15.1	1.1	
$p4$	38.0	18.5	-	218.31
$p4mm$	38.9	19.0	-	
$p4gm$	63.3	39.9	2.4	
$p3$	16.1	9.2	-	1.07
$p3m1$	17.4	10.9	-	
$p31m$	17.4	13.3	-	
$p6$	16.1	14.3	-	
$p6mm$	17.4	15.0	-	

the experimental data. This highlights a limitation of the CIP application of the geometric AIC procedure outlined in this paper.

10 Summary and Conclusions

CIP requires the user to choose one of the 17 crystallographic plane symmetry groups which best models an experimental image. Traditional methods of making this decision are not fully objective. This is because the 17 plane symmetry groups are not all disjoint. The geometric AIC is a useful statistical criterion for objectively determining the best geometric model from a group of non-disjoint models.

We adapted a geometric AIC algorithm from the robotics community (which was originally used to classify an arbitrary quadrilateral as a particular type of quadrilateral with at least the symmetry of a trapezoid) to determine which 2D Bravais lattice most closely models the lattice in an experimental, 2D periodic image. We showed, using a variety of real STM images of 2D periodic arrays, that this application of the geometric AIC can be used to help confidently choose one of the 17 plane symmetry groups in the CIP procedure when traditional methods fail to do so. This technique is complimentary to traditional symmetry determination in CIP in that the traditional figures of merit focus on the average motif in an image. On the other hand, this technique only determines the favored 2D Bravais lattice, not the plane symmetry group itself, so it is best used in conjunction with traditional CIP figures of merit.

Future work should aim to develop a geometric AIC algorithm compatible with the 17 plane symmetry groups themselves. Such an algorithm should be capable of removing subjectivity in determining plane symmetry in images altogether. Some progress has

already been made in this direction, as a geometric AIC procedure has been developed for classifying experimental data from patterns as one of the 7 crystallographic frieze groups, discussed in Appendix C.

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Appendix A: Calculation of Residuals for Geometric AIC

Here we calculate the residual J , to be used in conjunction with the geometric AIC (Equation (8.13)) for the purpose of choosing the 2D Bravais lattice which best models the lattice in an experimental 2D image. We look at the differences in the positions of vertices of a ‘model shape’, compared to the vertices of an ‘experimental’ shape. The experimental shape is determined by the lattice detected in the experimental image. The unit cell of a CIP enforced $p1$ image is just the translational averaged unit cell. The shape of this unit cell (which has at least the symmetry of a parallelogram) will serve as the starting point for determining our experimental shape.

We assume that every peak in the FT magnitude map is a measured point with variance proportional to the size of the peak (width in both directions in the hk -plane). In Figure A.1 we have a close-up of a typical Fourier peak, along with a plot of pixel intensity along a line passing horizontally through the peak. These intensities are fitted quite well with a sinc function, and so we assume that noise in the measurement of the peak position is independent Gaussian noise of mean zero and variance σ^2 . If the measurement of a Fourier coefficient peak obeys a normal distribution, so too will the positions of the lattice vectors which define our unit cell in both reciprocal and real space, and so it can be shown that J/σ^2 obeys a χ^2 distribution.

Therefore, we can create a trapezoid by shifting one of the vertices of our $p1$ unit cell

FIGURE A.1: Close-up of pixels around FT peak (left) and a plot of pixel intensity along a horizontal line through the peak (right) with fitted sinc function. The pixel intensity obeys an approximately normal distribution. Image from [62].

shape, determined by the variance of the corresponding reciprocal lattice vector. This trapezoid will serve as our experimental shape. Different sets of lattice parameters, gleaned from enforcing different plane symmetries on the experimental image in CIP, will define our model shapes. For instance, the lattice parameters resulting from enforcing group $p4mm$ will define our square model, the parameters resulting from enforcing group $p6mm$ will define our rhombus (with interior angles of 60° and 120°) model, etc. Because all of the models have at least the symmetry of a parallelogram, two vectors and the angle between them (i.e. the lattice parameters) is enough to fully define the shape.

Now that we have clarified how we define our experimental shape and model shapes, we move on to actually calculating the residual J . The first step is to find the vector

difference between corresponding vertices of our model and experimental shapes. To do this, we place one vertex at the origin of a Cartesian coordinate system, and one side of the shape (defined by lattice parameter $\mathbf{a}$) along the horizontal ($\hat{x}$) axis. Figure A.2 illustrates the positions of vertices for an arbitrary model. We use prime notation for our model shapes to differentiate from the experimental shape, whose orientation is similarly defined, just without the primes.

FIGURE A.2: Illustration of how a quadrilateral with at least the symmetry of a parallelogram is defined by just three parameters a' , b' and γ' , which are output from the general CIP procedure. We always set a vertex at the origin and the side corresponding to a' along the horizontal axis. These equations are the same for calculating the residuals for any of our models. Only the values of the 6 lattice parameters change.

The vector differences between the vertices of the experimental and model shapes are illustrated in Figure A.3. The solid (blue) line would represent a model (square in this example) and the dashed (red) line would represent the experimental shape. The vector difference is then just:

$$d_i = x_i - x_i' \tag{A.1}$$

where the x_i and x'_i are as defined in Figure A.2. The residual J for the model is just the sum of the squares of these distances:

$$J = \sum_i d_i^2 = |d_1|^2 + |d_2|^2 + |d_3|^2 + |d_4|^2 \quad (\text{A.2})$$

FIGURE A.3: Illustration of the calculation of the vector differences between one of our model shapes, a square (blue-solid) and our experimental shape (red-dashed).

In practice, we do not just calculate one residual for each model, however. In fact, we calculate 16 different residuals for each model and average them. To accomplish this, we create a trapezoid (based off of the uncertainty in the FT peak position as described above) by shifting the position of all 4 vertices, one at a time, in 4

directions (determined by the lattice angle parameter), yielding 16 different trapezoids (experimental shapes) to compare a particular model to. The following pages show the calculation of the residual for an arbitrary model for each of the 16 trapezoids (2 for each figure using $\pm$ notation). The parameters k_i tell us how much the vertices are shifted along a particular axis and are determined by the uncertainty in the lattice vector along that axis.

$$\mathbf{x}_1 = 0$$

$$\mathbf{x}_2 = (a \pm k_1) \hat{x}$$

$$\mathbf{x}_3 = b \cos \gamma \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = 0$$

$$d_2 = (a \pm k_1 - a') \hat{x}$$

$$d_3 = (b \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$\begin{aligned} J_1 = & k_1^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 \pm a k_1 \mp a' k_1 - 2 a a' - 2 b b' \cos (\gamma - \gamma') \right] \\ & + 2 \left[(a b - a' b) \cos \gamma + (a' b' - a b') \cos \gamma' \right] \end{aligned}$$

$$\mathbf{x}_1 = 0$$

$$\mathbf{x}_2 = (a \pm k_2 \cos \gamma) \hat{x} \pm k_2 \sin \gamma \hat{y}$$

$$\mathbf{x}_3 = b \cos \gamma \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = 0$$

$$d_2 = (a \pm k_2 \cos \gamma - a') \hat{x} \pm k_2 \sin \gamma \hat{y}$$

$$d_3 = (b \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$J_2 = k_2^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 + (ab - a'b \pm ak_2 \mp a'k_2) \cos \gamma \right] \\ + 2 \left[(a'b' - ab') \cos \gamma' - 2aa' - 2bb' \cos (\gamma - \gamma') \right]$$

$$\mathbf{x}_1 = 0$$

$$\mathbf{x}_2 = a\hat{x}$$

$$\mathbf{x}_3 = (b \cos \gamma \pm k_3) \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = 0$$

$$d_2 = (a - a') \hat{x}$$

$$d_3 = (b \cos \gamma \pm k_3 - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$J_3 = k_3^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 + (ab - a'b \pm k_3 b) \cos \gamma + (a'b' - ab' \mp k_3 b') \cos \gamma' \right] \\ + 2 \left[-2aa' - 2bb' \cos (\gamma - \gamma') \right]$$

$$\mathbf{x}_1 = 0$$

$$\mathbf{x}_2 = a\hat{x}$$

$$\mathbf{x}_3 = (b \cos \gamma \pm k_4 \cos \gamma) \hat{x} + (b \sin \gamma \pm k_4 \sin \gamma) \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = 0$$

$$d_2 = (a - a') \hat{x}$$

$$d_3 = (b \cos \gamma \pm k_4 \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma \pm k_4 \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$J_4 = k_4^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 \pm k_4 b \mp k_4 b' \cos (\gamma - \gamma') + (ab - a'b) \cos \gamma \right] \\ + 2 \left[(a'b' - ab') \cos \gamma' - 2aa' - 2bb' \cos (\gamma - \gamma') \right]$$

$$\mathbf{x}_1 = \pm k_5 \hat{x}$$

$$\mathbf{x}_2 = a \hat{x}$$

$$\mathbf{x}_3 = b \cos \gamma \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = \pm k_5 \hat{x}$$

$$d_2 = (a - a') \hat{x}$$

$$d_3 = (b \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$J_5 = k_5^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 + (ab - a'b) \cos \gamma + (a'b' - ab') \cos \gamma' \right] \\ + 2 \left[-2aa' - 2bb' \cos (\gamma - \gamma') \right]$$

$$\mathbf{x}_1 = \pm (k_6 \cos \gamma) \hat{x} \pm (k_6 \sin \gamma) \hat{y}$$

$$\mathbf{x}_2 = a \hat{x}$$

$$\mathbf{x}_3 = b \cos \gamma \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = \pm k_6 \cos \gamma \hat{x} \pm k_6 \sin \gamma \hat{y}$$

$$d_2 = (a - a') \hat{x}$$

$$d_3 = (b \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$\begin{aligned} J_6 = & k_6^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 + (ab - a'b) \cos \gamma + (a'b' - ab') \cos \gamma' \right] \\ & + 2 \left[-2aa' - 2bb' \cos (\gamma - \gamma') \right] \end{aligned}$$

$$\mathbf{x}_1 = 0$$

$$\mathbf{x}_2 = a\hat{x}$$

$$\mathbf{x}_3 = b \cos \gamma \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a \pm k_7) \hat{x} + b \sin \gamma \hat{y}$$

$$d_1 = 0$$

$$d_2 = (a - a') \hat{x}$$

$$d_3 = (b \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a \pm k_7 - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$J_7 = k_7^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 + (ab - a'b \pm k_7 b) \cos \gamma + (a'b' - ab' \mp k_7 b') \cos \gamma' \right] \\ + 2 \left[\pm k_7 a \mp k_7 a' - 2aa' - 2bb' \cos (\gamma - \gamma') \right]$$

$$\mathbf{x}_1 = 0$$

$$\mathbf{x}_2 = a\hat{x}$$

$$\mathbf{x}_3 = b \cos \gamma \hat{x} + b \sin \gamma \hat{y}$$

$$\mathbf{x}_4 = (b \cos \gamma + a \pm k_8 \cos \gamma) \hat{x} + (b \sin \gamma \pm k_8 \sin \gamma) \hat{y}$$

$$d_1 = 0$$

$$d_2 = (a - a') \hat{x}$$

$$d_3 = (b \cos \gamma - b' \cos \gamma') \hat{x} + (b \sin \gamma - b' \sin \gamma') \hat{y}$$

$$d_4 = (b \cos \gamma + a \pm k_8 \cos \gamma - b' \cos \gamma' - a') \hat{x} + (b \sin \gamma \pm k_8 \sin \gamma - b' \sin \gamma') \hat{y}$$

$$\begin{aligned} J_8 = & k_8^2 + 2 \left[a^2 + a'^2 + b^2 + b'^2 + (ab - a'b \pm k_8 a \mp k_8 a') \cos \gamma + (a'b' - ab') \cos \gamma' \right] \\ & + 2 \left[\pm k_8 b \mp k_8 b' \cos (\gamma - \gamma') - 2aa' - 2bb' \cos (\gamma - \gamma') \right] \end{aligned}$$

Appendix B: ITC Tables for Holohedral Plane Symmetry Groups

The non-translation symmetry operation generators of the holohedral groups, as well as their positions within the unit cell, as defined by the IUCr conventions, are highlighted.

Oblique

2

$p2$

Patterson symmetry $p2$

$p2$

No. 2

Origin at 2

Asymmetric unit $0 \leq x \leq \frac{1}{2}; 0 \leq y \leq 1$

Symmetry operations

(1) 1 (2) 2 0,0

Generators selected (1); $t(1,0)$; $t(0,1)$; (2)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

General:

no conditions

Special: no extra conditions

2 e 1 (1) x,y (2) $\bar{x},\bar{y}$

1 d 2 $\frac{1}{2}, \frac{1}{2}$

1 c 2 $\frac{1}{2}, 0$

1 b 2 $0, \frac{1}{2}$

1 a 2 0,0

Maximal non-isomorphic subgroups

I [2] $p1$ (1) 1

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $p2$ ($a' = 2a$ or $b' = 2b$ or $a' = a + b, b' = -a + b$) (2)

Minimal non-isomorphic supergroups

I [2] $p2mm$ (6); [2] $p2mg$ (7); [2] $p2gg$ (8); [2] $c2mm$ (9); [2] $p4$ (10); [3] $p6$ (16)

II none

$c2mm$

No. 9

$2mm$

$c2mm$

Rectangular

Patterson symmetry $c2mm$

Origin at $2mm$

Asymmetric unit $0 \leq x \leq \frac{1}{2}; 0 \leq y \leq \frac{1}{2}$

Symmetry operations

For $(0,0)+$ set

(1) 1
(2) 2 $0,0$
(3) m $0,y$
(4) m $x,0$

For $(\frac{1}{2},\frac{1}{2})+$ set

(1) $t(\frac{1}{2},\frac{1}{2})$
(2) 2 $\frac{1}{2},\frac{1}{2}$
(3) b $\frac{1}{2},y$
(4) a $x,\frac{1}{2}$

Generators selected (1); $t(1,0); t(0,1); t(\frac{1}{2},\frac{1}{2});$ (2); (3)

Positions		Coordinates		Reflection conditions	
Multiplicity, Wyckoff letter, Site symmetry		$(0,0)+$	$(\frac{1}{2},\frac{1}{2})+$		
8 f 1	(1) x,y	(2) $\bar{x},\bar{y}$	(3) $\bar{x},y$	(4) $x,\bar{y}$	General: $hk: h+k=2n$ $h0: h=2n$ $0k: k=2n$
4 e $.m.$	$0,y$	$0,\bar{y}$			Special: as above, plus no extra conditions
4 d $.m$	$x,0$	$\bar{x},0$			no extra conditions
4 c 2 $. .$	$\frac{1}{2},\frac{1}{2}$	$\frac{3}{2},\frac{1}{2}$			$hk: h=2n$
2 b 2 $m m$	$0,\frac{1}{2}$				no extra conditions
2 a 2 $m m$	$0,0$				no extra conditions

Maximal non-isomorphic subgroups

I	[2] $c1m1 (cm, 5)$	(1; 3)+
	[2] $c11m (cm, 5)$	(1; 4)+
	[2] $c211 (p2, 2)$	(1; 2)+
IIa	[2] $p2gg (8)$	1; 2; (3; 4) + $(\frac{1}{2},\frac{1}{2})$
	[2] $p2gm (p2mg, 7)$	1; 4; (2; 3) + $(\frac{1}{2},\frac{1}{2})$
	[2] $p2mg (7)$	1; 3; (2; 4) + $(\frac{1}{2},\frac{1}{2})$
	[2] $p2mm (6)$	1; 2; 3; 4
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [3] $c2mm (a'=3a \text{ or } b'=3b) (9)$

Minimal non-isomorphic supergroups

I	[2] $p4mm (11); [2] p4gm (12); [3] p6mm (17)$
II	[2] $p2mm (a'=\frac{1}{2}a, b'=\frac{1}{2}b) (6)$

$p4mm$ $4mm$

Square

No. 11

 $p4mm$ Patterson symmetry $p4mm$ Origin at $4mm$ Asymmetric unit $0 \leq x \leq \frac{1}{2}; 0 \leq y \leq \frac{1}{2}; x \leq y$

Symmetry operations

(1) 1 (2) 2 $0,0$ (3) 4^+ $0,0$ (4) 4^- $0,0$
 (5) m $0,y$ (6) m $\bar{x},0$ (7) m $x,\bar{x}$ (8) m $x,\bar{x}$

Generators selected (1); $t(1,0)$; $t(0,1)$; (2); (3); (5)**Positions**Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

8 g 1 (1) x,y (2) $\bar{x},\bar{y}$ (3) $\bar{y},x$ (4) $y,\bar{x}$
 (5) $\bar{x},y$ (6) $x,\bar{y}$ (7) y,x (8) $\bar{y},\bar{x}$

General:

no conditions

Special:

no extra conditions

no extra conditions

no extra conditions

 $hk: h+k=2n$

no extra conditions

no extra conditions

Maximal non-isomorphic subgroups

I [2] $p411$ ($p4, 10$) 1; 2; 3; 4
 [2] $p21m$ ($c2mm, 9$) 1; 2; 7; 8
 [2] $p2m1$ ($p2mm, 6$) 1; 2; 5; 6

IIa none

IIb [2] $c4mg$ ($a'=2a, b'=2b$) ($p4gm, 12$)**Maximal isomorphic subgroups of lowest index**IIc [2] $c4mm$ ($a'=2a, b'=2b$) ($p4mm, 11$)**Minimal non-isomorphic supergroups**

I none

II none

$p6mm$

$6mm$

Hexagonal

No. 17

$p6mm$

Patterson symmetry $p6mm$

Origin at $6mm$

Asymmetric unit $0 \leq x \leq \frac{2}{3}; 0 \leq y \leq \frac{1}{3}; x \leq (1+y)/2; y \leq x/2$

Vertices $0,0 \quad \frac{1}{2},0 \quad \frac{2}{3},\frac{1}{3}$

Symmetry operations

(1) 1	(2) $3^+ 0,0$	(3) $3^- 0,0$
(4) 2 $0,0$	(5) $6^- 0,0$	(6) $6^+ 0,0$
(7) $m \ x,\bar{x}$	(8) $m \ x,2x$	(9) $m \ 2x,x$
(10) $m \ x,x$	(11) $m \ x,0$	(12) $m \ 0,y$

Generators selected $(1); t(1,0); t(0,1); (2); (4); (7)$

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

General:

no conditions

Special: no extra conditions

12	f	1	(1) x, y (4) $\bar{x}, \bar{y}$ (7) $\bar{y}, \bar{x}$ (10) y, x	(2) $\bar{y}, x - y$ (5) $y, \bar{x} + y$ (8) $\bar{x} + y, y$ (11) $x - y, \bar{y}$	(3) $\bar{x} + y, \bar{x}$ (6) $x - y, x$ (9) $x, x - y$ (12) $\bar{x}, \bar{x} + y$
----	-----	---	---	---	---

6	e	$.m.$	$x, \bar{x}$	$x, 2x$	$2\bar{x}, \bar{x}$	$\bar{x}, x$	$\bar{x}, 2\bar{x}$	$2x, x$
6	d	$.m$	$x, 0$	$0, x$	$\bar{x}, \bar{x}$	$\bar{x}, 0$	$0, \bar{x}$	x, x
3	c	$2mm$	$\frac{1}{2}, 0$	$0, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$			
2	b	$3m.$	$\frac{1}{3}, \frac{2}{3}$	$\frac{2}{3}, \frac{1}{3}$				
1	a	$6mm$	$0, 0$					

Maximal non-isomorphic subgroups

I	[2] $p611 (p6, 16)$	1; 2; 3; 4; 5; 6
	[2] $p31m (15)$	1; 2; 3; 10; 11; 12
	[2] $p3m1 (14)$	1; 2; 3; 7; 8; 9
	{ [3] $p2mm (c2mm, 9)$	1; 4; 7; 10
	{ [3] $p2mm (c2mm, 9)$	1; 4; 8; 11
	{ [3] $p2mm (c2mm, 9)$	1; 4; 9; 12

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3] $h6mm (a' = 3a, b' = 3b) (p6mm, 17)$

Minimal non-isomorphic supergroups

I none

II none

Appendix C: Geometric AIC for Frieze Patterns

Here we follow the derivation of a geometric AIC criterion for the seven crystallographic frieze groups [63] as done by Liu et al. [64]. Patterns which adhere each of the frieze groups are shown in Figure C.1.

FIGURE C.1: Illustration of the 7 crystallographic frieze groups, using the notation of the ITC (left) and that of reference [64] (right). Image adapted from: http://en.wikipedia.org/wiki/Frieze_group.

An observed, nearly symmetric frieze pattern defined by pixel intensity variations, $\{p_i\}$, is orthogonally projected onto a manifold corresponding to its ‘perfect’ frieze tile composed of $\{q_i\}$. The perfect frieze tiles are defined such that the following distance measure is minimized [64, 65]:

$$SD = \sum_{i=1}^{tN} \left(\frac{p_i - q_i}{\sigma_i} \right)^2 \quad (\text{C.1})$$

where the frieze pattern is made up of t ‘tiles’ containing N pixels each (i.e. t repeats of the 2D subperiodic unit cell), p_i and q_i are the intensity values at pixel i , and σ_i is the standard deviation for the pixel noise model at pixel i for independent Gaussian noise of mean zero. This distance measure is subject to a χ^2 distribution with tN degrees of freedom.

We can use the geometric AIC to compare the symmetry distance measures for different frieze groups for the purpose of model selection, just as we did for the quadrilaterals. If we treat each pixel in the pattern independently as a 1 dimensional variable (with 1 degree of freedom corresponding to intensity variations of the pixel), a model will constrain the values to a 0 dimensional manifold (a point) in multidimensional intensity space. Hence, we get $d_1 = d_2 = 0$, and co-dimension $r = 1 - 0 = 1$. Substituting these values, along with tN for the total number of degrees of freedom for our pattern into Equation (8.10) yields the following, which is equivalent to Equation (2) in [64]:

$$\frac{SD_2}{SD_1} < 1 + \frac{2(n_1 - n_2)}{tN - n_1} \quad (\text{C.2})$$

where SD_1 and n_1 are the symmetry distance measure between a frieze pattern model and an experimental pattern, and the degrees of freedom of the model, respectively. SD_2 and n_2 are the same quantities corresponding to a frieze pattern model that is more symmetric. The degree of freedom is just the number of pixels in an image N , divided by the number of constraints on the model. The inclusion relation diagram for the frieze patterns are shown in Figure C.2, along with the constraints on the pixel

intensities and the corresponding degrees of freedom for each frieze group. Figure C.3 is an excerpt from the ITC Volume E showing one of the 7 subperiodic frieze groups. Applications of this geometric AIC could include its implementation into a procedure for detecting frieze group symmetry in images along grain boundaries to quickly classify such boundaries.

FIGURE C.2: (a) Inclusion relation diagram for the frieze groups, with degrees of freedom listed on the left. (b) General position diagrams showing the constraints on the 6 higher symmetric frieze groups' pixel intensity within a tile. The format of these diagrams does not follow the conventions of the ITC. An example page from reference [63], which includes the general position diagrams is shown below in Figure C.3. (Image taken from [64]).

FIGURE C.3: Example page from ITC Volume E, reference [63], showing the general position diagram for the frieze group corresponding to F1 in Figure C.2.