The Diffraction Pattern Calculator (DPC) toolkit: a user-friendly approach to unit-cell lattice parameter identification of two-dimensional grazing-incidence wide-angle X-ray scattering data

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The *DPC* toolkit is a simple-to-use computational tool that helps users identify the unit-cell lattice parameters of a crystal structure that are consistent with a set of two-dimensional grazing-incidence wide-angle X-ray scattering data. The input data requirements are minimal and easy to assemble from data sets collected with any position-sensitive detector, and the user is required to make as few initial assumptions about the crystal structure as possible. By selecting manual or automatic modes of operation, the user can either visually match the positions of the experimental and calculated reflections by individually tuning the unit-cell parameters or have the program perform this process for them. Examples that demonstrate the utility of this program include determining the lattice parameters of a polymorph of a fluorinated contorted hexabenzocoronene in a blind test and refining the lattice parameters of the thin-film phase of 5,11-bis(triethylsilylethynyl)anthradithiophene with the unit-cell dimensions of its bulk crystal structure being the initial inputs.

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1. Introduction

Owing to their light weight, low cost and amenability to facile processing methods, organic semiconductors are opening the door to new technologies, such as organic photovoltaics (OPVs), thin-film transistors (TFTs) and flexible electronic devices (Loo *et al.*, 2007). In particular, OPVs have attracted significant interest for their promising ability to harness solar energy (Müller-Buschbaum, 2014). The potential of these emerging technologies has spurred research to develop new electrically active materials that demonstrate improved electronic properties. In addition to the chemical structure, the morphology of organic semiconductor thin films is known to strongly influence electrical performance. Because charge carriers selectively transport through the π - π orbital overlap of neighboring molecules, the manner in which organic semiconductor molecules are packed and oriented within thin films has been shown to critically impact device performance (Lee & Loo, 2010). The way in which these organic semiconductors crystallize can vary based on their chemical functionalization, the pre- and post-deposition processing steps, and the influence of any additional constituents that are present in blends (Hiszpanski & Loo, 2014). For example, the self-organization of donor and acceptor materials in bulk heterojunction (BHJ) active layers of OPVs is extremely complex, and optimizing the blend morphology can lead to higher solar cell efficiencies (Müller-Buschbaum, 2014). Finally, given that these thin films are often only several hundred nanometres thick, molecule-substrate interactions can also often dominate structure development, leading to preferentially edge- or face-on molecular orientations that can also have profound effects on device performance.

Thus, understanding the processing-structure-function relationships of these compounds, and ultimately learning to control their

thin-film morphology, is critical for realizing the full potential of these emerging technologies (Chen *et al.*, 2012; Li *et al.*, 2012). Yet, determining the structure of these organic semiconductor thin films – of which the crystal structure is one of the most important aspects – remains challenging. Single-crystal diffraction is the most precise and direct way to determine an unknown crystal structure. Unfortunately, growing a suitably large and perfect sample can be technically challenging. Furthermore, some polymorphs only exist in thin films; these polymorphs may not form single crystals readily. Examples of organic semiconductors that exhibit thin-film phases that are structurally distinct from their bulk include pentacene (Dimitrakopoulos & Malenfant, 2002; Schiefer *et al.*, 2007) and 6,13-bis(triisopropylsilylethynyl)pentacene (Mannsfeld *et al.*, 2011). In thin films of binary blends, such as the active layers of BHJ OPVs, the constituents can also form co-crystals whose structure is completely different from those of the neat constituents. There thus remains a strong need to be able to extract unit-cell parameters from X-ray diffraction data collected directly on the polycrystalline thin films that represent the active layer structure of organic electronic devices.

2. GIWAXS features

Two-dimensional grazing-incidence wide-angle X-ray scattering (two-dimensional GIWAXS) is a method uniquely poised for investigating the morphology of thin films, such as the active layers of TFTs and OPVs, whose final film structure is highly sensitive to the preceding processing steps, materials involved and the processing conditions (Chen *et al.*, 2012; Müller-Buschbaum, 2014; Ree, 2014). As a nondestructive technique, GIWAXS can be used to track kinetically

the structural development of these thin films throughout film preparation (Müller-Buschbaum, 2014). By carefully choosing the grazing-incidence angle to be above the critical angle of the film but below that of the substrate, two-dimensional GIWAXS is capable of probing the ensemble-average microstructure of thin films that are approximately 100 nm thick (Smilgies *et al.*, 2005; Breiby *et al.*, 2008; DeLongchamp *et al.*, 2011; Fumagalli *et al.*, 2012).

Organic semiconductor thin films often comprise crystalline domains that are preferentially oriented; sometimes these thin films can contain populations of crystalline domains with distinctly different preferential orientations, each aligning with a different crystallographic plane parallel to the substrate (Smilgies *et al.*, 2000; Smilgies & Blasini, 2007; Resel, 2008; Li *et al.*, 2012). It is thus important to discern the parallel planes, *i.e.* planes that are parallel to the substrate, during the analysis of such X-ray diffraction data. In the fiber diffraction community, the direction perpendicular to this parallel plane (also the substrate normal) is known as the fiber axis. Increasingly, this nomenclature has been extended to describe preferential orientation in the out-of-plane direction in organic semiconductor thin films as well (Breiby *et al.*, 2008; Oh *et al.*, 2009). While these films show preferential orientation in the out-of-plane direction, the crystalline domains need not show preferential orientation in plane about the fiber axis. Sampling the diffraction of the crystallites that are randomly oriented in plane allows the capture of all allowed reflections within a given q -space range, much like the effect of rotating a single crystal during single-crystal diffraction measurements (Warren, 1969). If the films have lateral texture, meaning that they possess preferential orientations both in plane and out of plane, they can be rotated around their surface normal during data acquisition in order to capture all allowed reflections (Smilgies & Blasini, 2007). GIWAXS can thus be used to confirm the crystal structure and determine the orientation of crystallites in textured thin films. When a standard or calibrant is provided and the instrumental resolution is properly accounted for (Smilgies, 2009), GIWAXS can also provide information on the extents of crystallinity of these films with regard to average grain size and mosaicity (Breiby *et al.*, 2008; Huang *et al.*, 2009; DeLongchamp *et al.*, 2011; Kline *et al.*, 2011; Rivnay *et al.*, 2011; Chen *et al.*, 2012).

In the most general case, a unit cell is defined by three lattice dimensions and three angles that can, in principle, be independent of each other. Thus, solving the GIWAXS pattern for an unknown crystal structure is not an easy task. While programs exist to help users solve the unknown crystal structure given diffraction data, these programs were developed to analyze data derived from diffraction in geometries other than grazing incidence, such as diffraction in transmission (Liu *et al.*, 2012; Send *et al.*, 2012). Yet other programs focus on solving crystal structures from powder or single-crystal diffraction instead of from polycrystalline thin films (Neumann, 2003; Le Bail, 2004; Dinnebier *et al.*, 2006; Gruene *et al.*, 2014; Oliveira & Driemeier, 2013). Very few programs have been developed specifically for processing, or can be made compatible with, two-dimensional GIWAXS data (Salzmann & Resel, 2004; Smilgies & Blasini, 2007; Breiby *et al.*, 2008; Fuentes-Montero *et al.*, 2011; Mannsfeld *et al.*, 2011; Fumagalli *et al.*, 2012). This challenge stems from the need to account for azimuthally anisotropic intensities in such patterns, arising from the presence of preferentially oriented crystallites. Also challenging is the fact that the scattering volume in such thin films is small compared with those of single crystals or in the bulk. This experimental limitation often results in diffraction patterns with many fewer, weaker and broader reflections over a smaller q range than those found in single-crystal or powder diffraction patterns. Another difficulty arises when using a flat area detector to capture

thin-film diffraction within the reflection geometry; these detectors cause image distortion along the meridian, making quantitative analysis of orientation distribution more challenging (Baker *et al.*, 2010).

The *DPC* toolkit is a simple and user-friendly computational tool to help users identify unit-cell lattice parameters that are consistent with their two-dimensional GIWAXS data. Although organic semiconductor structural characterization motivated the development of this tool, the *DPC* toolkit was developed to be maximally flexible and can be used to analyze the structure of a myriad of organic thin films. This program is useful for analyzing diffraction patterns with reflections having azimuthally anisotropic intensities taking the form of many well defined peaks, or narrow arcs, as opposed to diffuse rings. The most general forms of calculations were used so that the program can analyze data derived from unit cells adopting any of the seven lattice systems. Put simply, the *DPC* toolkit tunes the unit-cell lattice parameters to produce calculated peaks whose positions match those of the experimental peaks based on a pre-specified parallel plane.

The *DPC* toolkit operates in either manual or automatic mode. In manual mode, the user visually matches the locations of the experimental and calculated peaks by altering the unit-cell parameters individually. In automatic mode, the program matches the positions of the experimental and calculated peaks for the user. In either mode, the *DPC* toolkit is not a black box; the program puts the tuning knobs into the hands of the user so that determining the unknown lattice parameters is an iterative learning process. The user is required to make as few initial assumptions about the crystal structure as possible, and experience will guide the user to narrow the phase space and promote convergence upon a reasonable solution.

3. Operating modes

The code for this program was written in MATLAB (The MathWorks Inc., Natick, MA, USA), a technical computing language and software package widely available at educational institutions. However, running this program does not require deep understanding of coding; users need only interact with graphical user interfaces (GUIs) and a simple parameter input form.

3.1. Manual

If manual mode is selected, a window displaying the experimental diffraction pattern will pop up. Fig. 1(a) shows an example of the manual mode window. Above the image, ten sliders controlling the unit-cell lattice parameters a , b , c , α , β and γ , the h , k and l Miller indices of the parallel plane, and the space group will appear. The user will set the initial values of these parameters in the parameter input form prior to running the code; the values for each of these parameters will be used to calculate the initial positions of the calculated peaks. The calculated peaks are then overlaid onto the experimental diffraction pattern. The user can vary the unit-cell parameters individually by adjusting the sliders in the window and see how the calculated peaks respond to these changes, accordingly.

3.2. Automatic

Automatic mode identifies the positions of the experimental peaks in the input diffraction pattern image and tunes the unit-cell lattice parameters (a , b , c , α , β and γ) to produce calculated peaks whose positions in q space fall within the area of an experimental peak. The program maximizes the intensity function in order to optimize convergence of the calculated diffraction pattern with the experimental diffraction pattern. The intensity function is the sum of

intensities calculated under the following conditions. For each calculated peak that is located within the area of an experimental peak, the intensity in the experimental diffraction pattern image around that calculated peak (averaged over a 3×3 pixel grid) is summed. To simultaneously discourage the program from erroneously calculating a unit cell that has reflections in regions of low intensity in the input image, a penalty is imposed on the intensity function for each calculated peak that is not located near an experimental peak. This strategy encourages the program to calculate a unit cell that yields peaks that fall only in areas of high intensity in the experimental diffraction pattern. This approach is also robust in cases where multiple peaks are within close proximity of each other.

The program optimizes the unit-cell lattice parameters by first performing a coarse fit to the data and then a fine fit. During the

coarse fit, the program calculates the intensity function for a number of random unit cells that fall within the user-specified boundaries for each unit-cell lattice parameter. For the fine fit, the program chooses the unit cell yielding the highest intensity function from the coarse fit, and then fine-tunes the unit-cell lattice parameters to further maximize the intensity function. When the program has completed the optimization process (finding a result within a tolerance of 1×10^{-4} or after 1200 iterations), a window displaying the experimental diffraction pattern will pop up. On top of this image, the program will plot the calculated peaks of the optimized unit cell; above the image, the program will list the associated lattice parameters and report the match quality. We are not able to use the more conventional R factor to quantify the quality of the fit, because quantification of the R factor relies on differences in the observed and calculated structure factors, which our program does not consider. Instead, we report the match quality, which quantifies the quality of the fit based on the positions (but not intensities) of the observed and calculated reflections. The match quality is calculated as the percentage of the experimental peaks that were found. An experimental peak is found if the position of a calculated peak lies within the peak area of the experimental peak.

Owing to the randomization and finite number of trials in the coarse fit, and the large number of possible parameter combinations, the program will often converge on a slightly different unit cell each time the program is run, even when the user does not change the input parameters. Running the program several times will help the user develop intuition about which parameter values yield the highest match quality; the user may then further confine the parameter ranges to help the program converge on these higher-quality matches more consistently. Fig. 1(b) shows an example of this window after the program had been run in automatic mode.

Figure 1
Screen shots of the graphical user interface window in (a) manual and (b) automatic modes providing lattice parameters for 2,8-difluoro-5,11-bis(triethylsilyl-ethynyl)anthradithiophene, F-TES ADT, based on a diffraction pattern of its thin film (also shown). Reflections associated with a different orientation of F-TES ADT were not considered in the optimization of the unit cell. Magenta circles highlight the placements of peaks calculated with (001) as the parallel plane.

4. Data input requirements

The input data requirements are minimal and easy to assemble from any data set collected on any beamline or with any position-sensitive detector. Prior to using the *DPC* toolkit, the user should create an image of their diffraction pattern. The user can create the best quality image by performing background subtraction, removing any dead or hot pixels, and cropping it to the relevant q space of interest. The user should save their image as a MATLAB figure (in '.Fig' format). From this figure, the *DPC* toolkit will extract the x -axis data (q_{xy} in $\text{\AA}^{-1}$), the y -axis data (q_z in $\text{\AA}^{-1}$) and the image matrix (intensity in arbitrary units). The program will ignore any other information that had been saved with the figure, including titles, axes labels and font properties. This generic and simple data input requirement makes this program compatible with the diverse data sets acquired using different detectors and processing software.

5. Image processing

When the user starts the program, GUI windows will pop up to allow the user to set and save image properties for the diffraction pattern to be analyzed. On subsequent runs of the same image, the user can elect either to apply these saved settings and bypass the image property pop-up windows or to create new settings. Fig. 2 shows examples of the image property settings windows. As shown in Fig. 2(a), on the basis of the operation mode selected by the user, the user will be asked to set up to six image property parameters, including the mask width, mask height, color scale min, color scale max, peak threshold and peak area.

Figure 2

Image property settings windows containing a diffraction pattern of a thin film of 2,8-diethyl-5,11-bis(triethylsilylethynyl)anthradithiophene. The window in (a) shows the diffraction pattern with the program's default settings. In (b), the settings for mask width and mask height have been increased, as seen by the dark ellipse now covering the area of high intensity near the beam center. The settings for 'color scale min' and 'color scale max' have been adjusted to increase the image contrast, as seen by the enhanced brightness of the peaks and darkness of the background. The settings for 'peak threshold' and 'peak area' have been increased to boost the selectivity of peak identification, removing the spurious peaks along $q_{xy} = 0.4 \text{ \AA}^{-1}$. The subsequent window in (c) shows the removal of an irrelevant and incorrectly identified peak at $q_z = 1.2 \text{ \AA}^{-1}$.

The mask settings allow the user to specify the size of a dark ellipse to block any extraneous intensity that results from main-beam bleeding over the beamstop (of radii mask width and mask height) at the beam center. These settings prevent the program from mistaking extraneous intensities from the main beam as diffracted intensities in the experimental diffraction pattern. The color scale settings control the contrast of the image: increasing 'color scale min' will make the dark regions of the image darker, while decreasing 'color scale max' will make the light regions of the image lighter. These settings allow the user to fine-tune the color contrast to ensure that all relevant experimental peaks are clearly visible. The peak settings are used to help the program identify the peaks in the experimental diffraction pattern; the program will try to match its calculated peaks to the positions of the identified experimental peaks in automatic mode. Increasing the peak threshold increases the relative intensity cutoff that the program uses to identify experimental peaks from local background intensity. Increasing the peak area increases the minimum size of a region the program considers an experimental peak (to avoid misidentifying any stray bright pixels as experimental peaks).

There thus exists a sweet spot between the color scale and peak settings in order to properly identify all of the relevant experimental peaks. If the color contrast is set too high, weaker experimental peaks may fade into the background, and the more intense experimental peaks may smear together. If the color contrast is set too low, the background noise will be high, and there could potentially be many regions misidentified as experimental peaks. The peak threshold and peak area may be increased to boost selectivity, but if these settings are set too high, one risks not identifying all relevant experimental peaks.

As demonstrated in Fig. 2(b), the user should tune these image property settings so that all relevant experimental peaks in the diffraction pattern are identified, even if these settings cause undesired areas to be identified as peaks initially. As shown in Fig. 2(c), the user will have the opportunity to remove any irrelevant regions of high intensity by manually selecting them out in a later window. Examples of regions of high intensity that should be removed prior to analysis include experimental peaks that result from a population of crystalline domains having the same unit cell but oriented differently (so a different parallel plane input would be required to capture these peaks) or experimental peaks that result from stray specks of silicon or glass upon the film (and are thus not representative of the crystal structure of the thin film under analysis).

6. Operating parameters

6.1. General settings

In order to reduce the number of assumptions the user must make about the unknown crystal structure, the program does not attempt to calculate structure factors. Calculating the structure factor (and therefore relative intensities of the peaks) of any reflection presupposes knowledge of the atomic (molecular in our case) coordinates in the unit cell. Thus, while the program attempts to identify a unit cell whose calculated peak positions match those of the experimental peaks, the program does not attempt to calculate peak intensities or match them to those of the experimental peaks. Instead, the user may choose the space group of the unit cell. Each space group has a set of index rules that dictate which reflections are allowed on the basis of the symmetry of the unit cell. Applying these general conditions avoids the calculation of any peaks associated with forbidden reflections, *i.e.* those whose structure factors are systematically zero.

It is important for the user to realize that, while the unit cell on which the program converges will produce a diffraction pattern that is consistent with the experimental data, this unit cell may not be unique. If the user requires a more rigorous analysis, the output from this program can, in turn, be used as input in more sophisticated or specialized crystal structure analysis programs which focus on minimizing crystal energy (DeLongchamp *et al.*, 2011) or for mean-square fitting (Breiby *et al.*, 2008).

Prior to running any unit-cell calculations, the user must set several general operating parameters in the *DPC* toolkit's script in the MATLAB editor window. In this program, the positions of the calculated peaks are determined using the method described by Smilgies & Blasini (2007). As input, this method requires initial guesses for the unit-cell plane that is parallel to the substrate, the range of each of the Miller indices of reflections, and the values of the unit-cell lattice parameters. As the symmetry of the Ewald sphere is broken by the presence of a substrate in grazing-incidence geometry, identifying the parallel plane helps to specify the azimuthal positions of the calculated peaks. If the bulk crystal structure of the sample is known, this often yields a good starting point for identifying the parallel plane of the thin-film phase. If the parallel plane of the unit cell is not known, the user should choose a low-index plane, such as (001) or (100); this selection may lead to the solution of a nontrivial surface unit cell, if not the solution of the most primitive unit cell (for examples, see Smilgies *et al.*, 2000; Krause *et al.*, 2001). Prior to analysis with this program, the user should check the experimental diffraction pattern for any evidence of multiple preferential orientations stemming from distinct populations of crystalline domains. One straightforward approach to accomplish this task is to replot the diffraction pattern as *q* versus azimuthal angle. The presence of multiple populations of differently oriented crystallites will result in each reflection appearing at multiple azimuthal angles at any given *q*. As this program allows the user to choose a single parallel plane, the user should remove any experimental peaks that do not correspond to this particular orientation before proceeding.

The set of reflections allowed by symmetry is calculated in two steps. First, the user chooses the range of *hkl* values for the program to consider, setting the ranges of *h*, *k* and *l* separately. The program then computes all possible permutations of these *hkl* values as Miller indices for all possible planes. Next, the user chooses the space group of the unit cell. The program then evaluates all the possible permutations of reflections based on the *h*, *k* and *l* ranges specified and removes any reflections that are forbidden because of symmetry in the lattice structure of the specified space group. Only general reflection conditions are considered, *i.e.* rules that are always obeyed regardless of which lattice positions are occupied in the unit cell. The program thus assumes that no special positions, which can impose additional restrictions on the allowed reflections, are occupied in the unit cell. We checked the quality of this assumption against the existing database of known crystal structures published by Wilson (1993). Given that molecules do not occupy any special positions in over 80% of the known triclinic, monoclinic and orthorhombic crystal structures, we feel that this assumption is valid in the basic evaluation of organic thin films that exhibit any of the common unit cells. Although this assumption is not equally valid for each space group, the occupation of special positions does not introduce any additional reflection conditions in many cases (Aroyo *et al.*, 2006). Our decision to only consider general reflection conditions thus greatly simplifies our calculations without the need to sacrifice accuracy. If the space group of the unit cell is unknown, the user should start with a space group that allows all reflections and then check for systematic absences of reflections in the experimentally obtained diffraction

pattern to narrow down the qualifying space groups. Alternatively, the user can initially guess a common space group. *P2₁/c* is one such common space group that is adopted by 34.8% of small molecules (Allen, 2002; Price, 2014).

The user must also set the ranges of the individual unit-cell lattice parameters by specifying the minimum and maximum values. The unit-cell lengths are independent quantities and thus may take any positive value greater than zero. This constraint, however, is not true for the unit-cell angles. Although each individual angle may theoretically take any value between 0 and 180°, the angles may not be defined independently, and forbidden combinations result in null or imaginary unit-cell volumes (Foadi & Evans, 2011). Generally, a range of 60–120° for α , β and γ is sufficient to define a unit cell, and this limited range reduces the possibility of accessing a forbidden combination (Hahn, 2002). The program further checks that all optimized unit-cell lattice parameter combinations result in real solutions.

The user can also choose to enable plot labels, in order to display the Miller index associated with each calculated peak in the final solution window. Finally, the user can choose to output to the command window the positions of the calculated peaks labeled by their Miller indices as well as the unit-cell lattice constants of the predicted unit cell.

6.2. Additional considerations and settings for manual mode

The specifications in the general settings become the initial values or ranges of parameters in manual mode. In addition to these general settings, the user must specify the initial guesses for the unit-cell lattice parameters, which also serve as the initial positions of these sliders in the manual mode window. The user may choose to specify these values manually or to have the program set the values as the median of the range set for each lattice parameter. The specified Miller index for the parallel plane, space group and lattice parameters are then used for determining the initial positions of the calculated peaks. The user will be able to see how the positions of the calculated peaks respond to changes in these unit-cell parameters by subsequently adjusting the values of these parameters with the sliders in the manual mode window. During the course of program operation, if the user slides through a parameter combination that results in an unphysical unit-cell volume, the program will not plot any calculated peaks on the experimental diffraction pattern until the user manually slides the parameters back to values that can result in real solutions. With a checkbox that the user may turn on or off, the user can choose to display the Miller indices associated with the calculated peaks. After the user closes the manual mode window, the program will display the final parameter settings in the command window.

6.3. Additional considerations and settings for automatic mode

The program will remove any calculated peaks whose positions fall outside the range of experimental peaks. Thus, in the general parameter settings, the user should set the range of *hkl* values at least as high as the order of reflections that can be observed in the diffraction pattern, but not unnecessarily high, as this will reduce program speed. For example, in Fig. 1, three strong peaks are observed in the diffraction pattern along the meridian at $q_{xy} = 0$. As this diffraction pattern corresponds to a triclinic crystal structure where there is no symmetry to cause forbidden reflections, the range of *h*, *k* and *l* should be set to at least three. If, however, the diffraction pattern corresponded to a more symmetrical crystal structure that forbids, for example, odd-numbered reflections along the meridian, the range of *h*, *k* and *l* should be set to at least six. Thus, the user should set the *hkl*

ranges based on the number of peaks observed along the meridian while taking into account any prior knowledge of the unit cell, such as the space group.

The ranges of the unit-cell lattice parameters defined in the general parameter settings are used to limit the searching algorithm for each unit-cell parameter. Thus, the ranges should be set as tight as possible to help the algorithm converge on the optimized unit cell. The size of a unit cell greatly depends on the number of molecules it contains. For example, consider the triclinic and monoclinic polymorphs of 5,11-bis(triethylsilylethynyl)anthradithiophene, TES ADT. The crystal structure of the triclinic polymorph contains only one molecule and the largest dimension is less than 20 Å (Payne *et al.*, 2005). The crystal structure of the monoclinic polymorph, on the other hand, is a superlattice comprising approximately 50 molecules, and the largest dimension is almost 100 Å (Lee, Loth *et al.*, 2012). Examples of other classes of materials that comprise yet more molecules include protein crystals, which can contain several hundred monomers, and their unit-cell lengths can span several hundred ångströms (Allen, 2002; Stewart *et al.*, 2008). As a lower limit for the unit-cell lengths, the user may take 2 Å as a reasonable assumption for typical molecular crystals (Hooft *et al.*, 1994).

Several additional parameters must also be set when running the program in automatic mode. First, the user must select a lattice system for the unit cell. This setting defines the relationships between the unit-cell lengths and angles. As specified in *International Tables for Crystallography*, the monoclinic lattice system in our program specifies the *b* axis to be the special axis and the angle β to be greater than 90°, while the tetragonal and hexagonal lattice systems assume the *c* axis to be the special axis (Allen, 2002). The program will enforce symmetry that is specified by the lattice system upon user inputs and its own results. For example, the user may only select a space group that matches the specified lattice system. Additionally, the user must set the ranges of the unit-cell lattice parameters so that they do not conflict with the conditions of the specified lattice system. As an illustration, if the lattice system is set to triclinic, the program verifies that $a_{\min} \leq b_{\min} \leq c_{\min}$ and $a_{\max} \leq b_{\max} \leq c_{\max}$.

Although triclinic would be the most inclusive guess, if the lattice system is not known, the user should start with a more restricted phase space by guessing a lattice system that exhibits higher symmetry. For example, choosing the orthorhombic system – adopted by 17.7% of all known crystal structures (Allen, 2002) – will let the unit-cell lengths vary while holding the unit-cell angles constant at 90°. This selection allows the program to focus on solving three parameters instead of six. Then with the tightened unit-cell length ranges in place, the user can select the monoclinic system as a second guess to let one of the angles float. The monoclinic system is the most common lattice system for organic molecules and is adopted by 52.3% of all known crystal structures (Allen, 2002). If no satisfactory results are obtained with these lattice systems, the user should then move on to the triclinic system – adopted by 25.1% of all known crystal structures (Allen, 2002) – to let all six parameters vary. In this way, the user can systematically sample the phase space and lattice symmetries that are adopted by more than 95% of all known crystal structures (Allen, 2002).

During the initial coarse fit when the program runs in automatic mode, the

program calculates the intensity function for a number of random unit cells that fall within the user-specified boundaries for each unit-cell lattice parameter. Thus, the user must specify the number of iterations, referred to as ‘trial runs’ in the program. Intuitively, the higher the number of trial runs, the more likely the program is to find a unit cell that yields calculated peaks whose positions are consistent with those of the experimental peaks. However, setting the number of trial runs overly high will necessarily require longer program run times. Given that the fine fit feature [which uses the Nelder–Mead simplex algorithm (Lagarias *et al.*, 1998) to maximize the intensity function] is capable of finding optimal results from less-than-optimal inputs, reducing the number of trial runs during the coarse fitting is not necessarily detrimental for convergence. On data sets we have tested (see below for select examples), trial runs numbering from 100 to 1000 for the coarse fits have yielded reasonable solutions in under 10 s.

6.4. Boundary tightening

The most important tool to help the program converge upon a reasonable unit cell when operating in automatic mode is boundary tightening. Boundary tightening narrows the guess ranges for the unit-cell lengths beyond the user-specified values. With the boundary-tightening algorithm guiding the search, the user can quickly develop intuition about a tighter range of possible unit-cell lengths. This optional feature is only available when the Miller index of the parallel plane of the predicted unit cell has been set to (001), (010) or (100). The algorithm uses the *q*-space positions of key experimental peaks to estimate the minimum and/or maximum values that are physically possible for the individual unit-cell lengths. The algorithm needs at least one experimental peak along $q_{xy} = 0$ (*i.e.* anywhere along the meridian) and at least one additional experimental peak at $q_{xy} > 0$.

In order to understand how boundary tightening works in real space, consider Fig. 3. For the purpose of this discussion, we shall assume that all experimental peaks are allowed. Fig. 3(a) shows a schematic of a unit cell with unit-cell lengths *a*, *b* and *c*, and unit-cell angles α (between *b* and *c*), β (between *a* and *c*) and γ (between *a* and *b*). For a conventional unit cell of any lattice system, α , β and γ are practically limited to a potential range of 60–120° (Hahn, 2002). In this example, we start with a cubic unit cell so *a*, *b* and *c* are equal, and α , β and γ are 90°. Fig. 3 shows the unit cell oriented with its (100) plane parallel to the substrate; thus, *a* measures the out-of-plane unit-cell length while *b* and *c* measure the in-plane unit-cell lengths and are equal in magnitude to *a*. We first focus our attention on the first-

Figure 3

Scheme depicting how boundary tightening functions in real space. View (a) shows a cubic unit cell with equal lengths *a*, *b* and *c*, and 90° angles for α , β and γ . View (b) shows that $a_{\min}$ occurs when β and γ are 90°, while $a_{\max}$ occurs when the (100) plane is sheared so that β and γ reach their extremes of 60° and/or 120°. Image (c) shows that $c_{\min}$ occurs when α is 90°, while $c_{\max}$ occurs when the (001) plane is sheared so that α reaches its extreme of 60° or 120°.

order reflection in the out-of-plane direction at $q_{xy} = 0$ for the corresponding X-ray diffraction pattern. Converting the q vector of this reflection to real space yields d_{100} . We can thus ask ourselves, under what conditions will d_{100} correspond to the minimum and maximum values of a , $a_{\min}$ and $a_{\max}$, respectively? From Fig. 3(b), we observe that d_{100} yields $a_{\min}$ when β and γ are 90° . To assess $a_{\max}$, we effectively have to shear the (100) plane. This action, shown in Fig. 3(b), allows us to maintain d_{100} and evaluate the conditions for which $a = a_{\max}$ for any given unit cell. To accommodate this shearing motion, β and γ will correspondingly need to shift from 90° . Assuming a conventional unit cell so β and γ are bound between 60 and 120° , we can determine the maximum value of a when β and γ are at either of their extremes.

Now we shift our focus to the reflections along $q_{xy} = \text{minimum} > 0$. This first column of reflections should yield information about the in-plane unit-cell lengths. As q space is inversely related to real space, a larger characteristic in-plane length will appear at smaller q_{xy} compared with a smaller characteristic in-plane length. Take for example a triclinic unit cell, where c must be greater than or equal to b . The first column of reflections along $q_{xy} = \text{minimum} > 0$ must thus correspond to the ($h01$) series of planes, from which c can be determined. The q_{xy} vectors of these reflections are equivalent and can be converted to real space to yield d_{001} . The minimum and maximum possible values of c can then be determined in the same fashion described above by shearing the (001) plane, as shown in Fig. 3(c). This action allows us to vary the angle α . In order to maintain the same d spacing as the (001) plane, $c_{\min}$ occurs when α is 90° , that is, when c is d_{001} . Shearing the unit cell along this plane, and thus varying the angle α from 90° , increases c . Accordingly, $c_{\max}$ occurs when α reaches its limits, at 60 or 120° . As for triclinic lattices the greatest possible value of b is c , we conclude in this case that $b_{\max} = c_{\max}$.

However, we cannot estimate $b_{\min}$ from the experimental diffraction pattern, because we are not able to identify which reflections correspond to the ($h10$) series of planes. Thus, the user is left to define a reasonable $b_{\min}$. For other lattice systems where either b or c may be the larger in-plane length, the previously described boundary-tightening strategy can be analogously applied to determine $b_{\max}$. In these cases, however, we are unable to estimate either $b_{\min}$ or $c_{\min}$; the user must thus either guess or estimate these values by other means.

When identifying the experimental peaks that occur at $q_{xy} = 0$ (along the meridian) and $q_{xy} = \text{minimum} > 0$, this algorithm takes into account any forbidden planes of the space group that are specified for the unit cell. For example, when the parallel plane is specified as (100), the program searches the set of allowed reflections for the minimum $h00$ reflection, and the q_z position of this peak is used to determine the minimum and maximum values of a . To determine the possible ranges for b and c , the program searches the set of allowed reflections for the minimum in k in the series of $hk0$ reflections and the minimum in l in the series of $h0l$ reflections, respectively. If any of these series of reflections are systematically absent due to symmetry constraints of the unit cell, the program will search for the next-highest series of reflections until the values of h , k and/or l reach their user-specified limits.

After the maximum and/or minimum values for the unit-cell lengths have been calculated, the program verifies whether the new boundary limits are less than or equal to the user-specified ranges for unit-cell lengths. If the boundary-tightening algorithm fails at any point, or if the determined limits are greater than the user-specified limits, the program will display a warning message and employ the user-specified boundary conditions instead. If the boundary-tightening algorithm is successful, the program will utilize the new boundary conditions instead of those specified by the user.

7. Examples

7.1. Refinement of the thin-film structure of TES ADT

The crystal structures adopted by thin films can often be influenced by the presence of the substrate and can therefore be different from that adopted by the same material in the bulk (Dimitrakopoulos & Malenfant, 2002; Schiefer *et al.*, 2007; Mannsfeld *et al.*, 2011; Witte & Wöll, 2011). The manual mode of the DPC toolkit lends itself to the refinement of the thin-film phase lattice parameters, particularly when the bulk phase crystal structure is known. Fig. 4 shows the refinement of the lattice parameters of the thin-film phase of TES

Figure 4

Refinement of the thin-film structure of 5,11-bis(triethylsilyl)ethynylanthradithiophene, TES ADT, using manual mode. In (a), the positions of the calculated reflections (magenta circles on the diffraction pattern) were determined based on the published single-crystal data for TES ADT (Payne *et al.*, 2005). In (b), the unit cell has been refined so that the calculated reflections more precisely match the experimental diffraction pattern. This structure is consistent with that found by Lee, Tang *et al.* (2012).

ADT, using manual mode. The bulk crystal structure of TES ADT was solved using single-crystal diffraction by Payne *et al.* (2005); the input values to the program for the space group (2, *i.e.* $P\bar{1}$) and unit-cell lattice parameters ($a = 6.73$, $b = 7.25$, $c = 16.69$ Å, $\alpha = 98.14$, $\beta = 94.53$, $\gamma = 103.92^\circ$) in Fig. 4(a) were taken from this reported structural information. We picked (001) to be the parallel plane based on our prior experience with other similar molecules: that such rod-like molecules tend to organize preferentially with their π planes normal to a noninteracting substrate (Chen *et al.*, 2007; Teague *et al.*, 2008; Lee, Loth *et al.*, 2012).

Fig. 4(a) plots the calculated peaks based on these input parameters on the experimental diffraction pattern. As evident in Fig. 4(a), the calculated peaks given the bulk crystal structure do not align well with the experimental peaks. This mismatch is most evident with the series of experimental peaks at $q_{xy} = 1.46$ Å⁻¹. In Fig. 4(b), the experimental and calculated peaks are brought into alignment by increasing a , b , c and γ , and decreasing α and β , using the sliders in manual mode. We find these new values to be $a = 6.91$, $b = 7.43$, $c = 16.91$ Å, $\alpha = 96.26$, $\beta = 92.09$, $\gamma = 105.94^\circ$. These thin-film lattice parameters are consistent with those found by Lee, Tang *et al.* (2012) using a similar best fit approach ($a = 6.92$, $b = 7.44$, $c = 16.75$ Å, $\alpha = 96.45$, $\beta = 91.96$, $\gamma = 105.60^\circ$). These new values indicate that the crystal structure of the thin-film phase of TES ADT is slightly larger along all dimensions than in its bulk crystal structure. (This increase in unit-cell volume could also be due to thermal expansion, as single-crystal diffraction is typically performed at liquid-nitrogen temperatures.) Similarly subtle differences between the bulk and thin-film phase crystal structures have also been reported for pentacene; the unit-cell lattice parameters of the bulk phase are $a = 6.06$, $b = 7.90$, $c = 15.01$ Å, $\alpha = 81.6$, $\beta = 77.2$, $\gamma = 85.8^\circ$, while the lattice parameters of the thin-film crystal structure are $a = 5.96$, $b = 7.60$, $c = 15.61$ Å, $\alpha = 81.3$, $\beta = 86.6$, $\gamma = 89.8^\circ$ (Campbell *et al.*, 1962; Nabok *et al.*, 2007; Schiefer *et al.*, 2007). In the case of pentacene, the crystal structure of the thin-film phase is slightly smaller along a and b , but larger along c compared with its bulk.

7.2. Determination of the unit-cell lattice parameters of 16F-HBC

In order to assess how well automatic mode can determine the lattice parameters of a crystal structure given an X-ray diffraction pattern, we conducted a blind test to solve for the lattice parameters of a fluorinated contorted hexabenzocoronene, 16F-HBC. Fig. 5

details the results of this investigation. As three strong peaks are observed in the diffraction pattern along the meridian at $q_{xy} = 0$, the range of h , k and l was set to three. We assumed (100) to be the plane in the unit cell that is parallel to the substrate. The ranges of the unit-cell lengths and angles were set to reasonable ranges of 2–40 Å and 90–120°, respectively. In order to systematically explore the influence of the unit-cell lattice constants, the lattice system was initially set to orthorhombic to hold the unit-cell angles constant at 90°. We assumed no special space-group symmetry and thus allowed all reflections. Boundary tightening was enabled; because all reflections were allowed, the q_z position of the 100 reflection was used to tighten the range of a from 12 to 18 Å, and the q_{xy} position of the $h10$ and $h01$ series of reflections was used to tighten the ranges of b and c from 2 to 10 Å. The number of trial runs was set to 100. Fig. 5(a) shows the solution generated in automatic mode under these conditions; the placements of the calculated peaks appear to agree well with those of the experimental peaks, with a match quality of 72%.

Next, the lattice system was set to monoclinic to let β float as we were interested in seeing how this change affected the calculated diffraction pattern. We again assumed no special space-group symmetry and thus allowed all reflections. Fig. 5(b) shows the solution generated in automatic mode when a monoclinic unit cell, instead of an orthorhombic unit cell, was specified. Although β can, in principle, vary between 90 and 120°, the program calculated β to be very close to 90°, and the optimized unit cell and calculated diffraction pattern are very similar to those originally calculated on the basis of the orthorhombic lattice system, with a match quality of 68%.

Finally, the space group was changed to 14 (*i.e.* $P2_1/c$), because this space group is the most common for organic small molecules. For the $P2_1/c$ space group, the $h01$ reflections are forbidden. Thus, in this case, the q_z position of the 100 reflection and the q_{xy} positions of the $h10$ and $h02$ series of reflections were used for boundary tightening. The boundary-tightening algorithm determined a to be 12–18 Å and $b_{\max}$ to be 10 Å as before. Here, $c_{\max}$ was estimated to be 20 Å using boundary tightening based on the $P2_1/c$ space group. Fig. 5(c) shows the solution generated in automatic mode under these conditions. The match quality here is 76%, the highest of the three cases; the improved fit can be seen most clearly by the experimental reflections now predicted to fall at $q_{xy} = 1.5$ Å⁻¹, $q_z = 0$ Å⁻¹ and along $q_{xy} = 2$ Å⁻¹.

For each of the three cases, the optimized unit-cell values listed in Table 1 differ by less than half an ångström or degree from the

Figure 5

Unit-cell lattice parameters determined by automatic mode for a diffraction pattern obtained from a thin film of fluorinated contorted hexabenzocoronene (16F-HBC). Reflections associated with a different orientation of 16F-HBC were not considered in the optimization of the unit cell. In (a), the user chose an orthorhombic lattice and a space group allowing all reflections. In (b), the user chose a monoclinic lattice and a space group allowing all reflections. In (c), the user chose a monoclinic lattice and the $P2_1/c$ space group.

Table 1

Unit-cell lattice parameters determined by automatic mode for the diffraction pattern under the conditions discussed in Fig. 5.

The values for α and γ were held constant at 90° for all cases and are thus not listed. With the space group correctly identified, the deviation of unit-cell length c from its actual value changes from over 6 Å to less than 0.1 Å. Values in italics indicate the difference from the value reported by Loo *et al.* (2010).

Unit cell	a (Å)	b (Å)	c (Å)	β ($^\circ$)
Loo <i>et al.</i> (2010)	12.9665	8.5663	14.3105	90.2706
(a) Orthorhombic	12.9273	8.5019	7.4413	90
<i>difference</i>	<i>0.0392</i>	<i>0.0644</i>	<i>6.8692</i>	<i>0.2706</i>
(b) Monoclinic	12.8449	8.4915	7.4339	90.0216
<i>difference</i>	<i>0.1216</i>	<i>0.0748</i>	<i>6.8766</i>	<i>0.2490</i>
(c) $P2_1/c$	12.9092	8.5252	14.3963	90.4946
<i>difference</i>	<i>0.0573</i>	<i>0.0411</i>	<i>-0.0858</i>	<i>-0.2240</i>

published unit-cell parameter values ($a = 12.9665$, $b = 8.5663$, $c = 14.3105$ Å, $\alpha = 90$, $\beta = 90.2706$, $\gamma = 90^\circ$), except in one dimension (Loo *et al.*, 2010). When all the reflections were allowed, c deviated from its published value by over 6 Å. However, by assuming the correct space group and parallel plane and applying these symmetry rules to the unit-cell calculations, the program converged upon a value that is consistent with that measured experimentally. Because we had correctly identified the parallel plane from the outset, the program compensated for the missing $h01$ reflections by doubling the length of c when the symmetry rules of the $P2_1/c$ space group were applied. If we had instead selected an incorrect parallel plane, the program would have adjusted a different unit-cell dimension. Even in automatic mode, it is thus important to examine the resulting fit carefully and take full advantage of the user's experience and intuition. In our hands, the DPC toolkit's automatic mode was able to predict the correct lattice parameters of the unit cell of 16F-HBC within a few iterations.

8. Conclusions

The DPC toolkit is designed to help users identify unit-cell lattice parameters of a crystal structure that are consistent with their two-dimensional GIWAXS data. It is an interactive tool to build intuition about the relationships between unit-cell parameters and their resulting two-dimensional GIWAXS diffraction pattern. This program can be used in a wide range of applications, from a first-pass effort to tackle the enormous phase space when solving a new crystal structure, to the refinement of the thin-film structure of a sample with a known crystal structure. This program is currently in use at the Organic and Polymer Electronics Laboratory at Princeton University, the Cornell High Energy Synchrotron Source, the University of Vermont, and the University of California, Santa Barbara. MATLAB is capable of running on Windows, Mac and Linux operating systems, and the DPC toolkit has been tested in versions R2011a, R2012a and R2013a. This program requires access to MATLAB's Optimization and Image Processing toolboxes. The latest edition of the program files and user's manual can be downloaded from <http://www.princeton.edu/cbe/people/faculty/loo/group/software>.

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