

Article

Indexing 2D Powders and Lagrange–Gauss Reduction

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Abstract

Two-dimensional (2D) powders constitute an important class of molecular thin films where a specific close-packed plane forms parallel to the substrate surface, while there is no preferred lateral ordering. Using results from classic lattice reduction theory, a systematic scheme is proposed in order to determine the 3D surface unit cell for 2D powders in reciprocal space. The approach is based on a sorted set of lengths $q_1, q_2, q_3, \dots$ of the in-plane components of the scattering vector, which is directly obtained from the scattering pattern. After a first match is established, a refinement procedure is presented that makes full use of the complete set of scattering vectors and, as such, corrects for small experimental errors and ensures a good overall match with the observed reflections. After identifying the in-plane components, the full 3D surface unit cell can be found in a straightforward way.

Keywords: molecular thin films; 2D powders; indexing; grazing incidence X-ray scattering

1. Introduction

A characteristic of functional thin films grown on smooth substrates, such as silicon wafers and glass slides, is that films crystallize with a specific crystallographic plane parallel to the substrate, while crystalline domains are randomly oriented laterally. Such 2D powders can be conveniently characterized with X-ray scattering techniques such as GISAXS or GIWAXS (grazing incidence small or wide-angle x-ray scattering, respectively), which make use of area detectors [1–5] or line detectors [4,6] and cover large parts of reciprocal space efficiently. While typically 10 to 50 reflections can be observed, this is by no means sufficient for an ab initio crystal structure determination. Nonetheless, usually the thin film lattice constants can be determined. In many cases the molecular lattice in the thin film is different from the bulk single crystal. Usually the structure of the molecule is known from single crystal diffraction, which is performed routinely after molecule synthesis. By determining the thin-film crystal lattice parameters, a rigid molecule approximation can be employed where the molecular structure is taken from single crystal data and then fit into the experimentally determined thin-film unit cell [7–9]. This way the molecular orientation on the substrate can be found, from which other properties, in particular the lateral and perpendicular charge mobilities, can be calculated and correlated with device performance.

Hence the determination of the thin-film molecular lattice, also known as indexing, is crucial for understanding the performance of molecular thin films [5,10–14]. Another fascinating aspect is polymorph control during thin-film processing [15–21]. In the following it will be discussed how to approach this problem for low-symmetry lattices that small molecules typically crystallize in and how insights from classical mathematics help to determine a compact surface unit cell.



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2. Methods

The idea for this paper originated in a series of brain-storming sessions with Google Gemini 2.5 and Anthropic Claude Sonnet 4.5 about how to uniquely define a “best” unit cell for a 2D lattice. This brought classical work on number theory and contemporary work on cryptography to the author’s attention that is usually not referred to in modern crystallography. The properties of the 2D reduced unit cell have important consequences for solving the indexing problem for 2D powders.

3. Results and Discussion

In this section important concepts such as surface unit cells and scattering rods are introduced, and then the indexing problem will be discussed and illustrated with examples.

3.1. Bulk and Surface Unit Cell in Real and Reciprocal Space

When molecules crystallize on a smooth substrate, they often choose a molecular layer inside the bulk structure to form a dense-packed layer parallel to the substrate surface. This can be a low-index Miller plane such as (001), but sometimes such molecular layers are formed in different planes inside the crystallographic unit cell, such as (201) [22,23]. In the latter case the lattice vectors of the surface unit cell do not coincide with the bulk lattice vectors. The surface unit cell has some interesting properties, which help to solve the indexing problem.

With two lattice vectors lying in the surface plane, this means that the reciprocal surface unit cell, constructed in the usual way from the real-space surface unit cell of a multilayered thin film, will have a vector $\vec{c}^*$ that is perpendicular to the reference surface. In contrast, the other reciprocal vectors will, in general, have components both parallel and perpendicular to the surface plane, in particular for triclinic lattices, where all angles between lattice vectors differ from 90° . Hence the indexing problem can be separated into finding the in-plane lattice parameters $\vec{a}_\parallel^*$, $\vec{b}_\parallel^*$ and the enclosed angle $\gamma_\parallel^*$ and then, as a second step, determining a solution for the perpendicular lattice parameters [5]. Here we will be mainly concerned with deriving the in-plane lattice parameters of the reciprocal surface unit cell.

3.2. Scattering Rods

For a 2D powder we established that the $\vec{c}^*$ reciprocal lattice vector is perpendicular to the substrate surface. The diffraction spots form lines along $\vec{c}^*$, the so-called scattering rods [23]. For stronger reflections one can also observe diffuse scattering streaks perpendicular to the surface, which originate from the truncation of the thin-film lattice at its surface [24,25]. Due to the nonlinear relationship between angular space and reciprocal space, the scattering rods often appear slightly curved in the detector image. However, with suitable software, the reflections along the rods can be extrapolated and so the in-plane q -vectors can be found, even if there are no reflections close to the horizon. This provides us with a sufficient number of in-plane scattering vectors, which will then be used for solving the in-plane lattice.

3.3. 2D Lattices and Lagrange–Gauss Reduction

A 2D lattice is given by two vectors $\vec{a}_\parallel^*$ and $\vec{b}_\parallel^*$ that are not colinear. Lattice points are given as

$$\vec{q}(h,k) = h \vec{a}_\parallel^* + k \vec{b}_\parallel^* \quad (1)$$

yielding for the squared lengths

$$q^2(h, k) = h^2 a_{\parallel}^{*2} + 2 h k a_{\parallel}^* b_{\parallel}^* \cos(\gamma_{\parallel}^*) + k^2 b_{\parallel}^{*2} \quad (2)$$

where $h, k \in \mathbb{Z}$ are integer numbers and $\gamma_{\parallel}^*$ is the enclosed angle between the parallel lattice vector components. We note that $q(1, 0) = a_{\parallel}^*$ and $q(0, 1) = b_{\parallel}^*$, i.e., $a_{\parallel}^*$ and $b_{\parallel}^*$ are contained within the set of lattice vectors, as is the origin. A well-known problem is that there is an infinite number of choices of $\vec{a}_{\parallel}^*$ and $\vec{b}_{\parallel}^*$ that can span the same lattice (see Figure 1). However, other than in higher dimensions, there is a well-defined way in two dimensions to uniquely extract a “best” choice of such vectors that was found in classic mathematics of the 18th century. Lagrange in 1773 and Gauss in 1801 independently encountered 2D lattices in the course of their studies on binary quadratic forms [26,27]. The Lagrange–Gauss algorithm can be easily described (see Figure 2): if there are two vectors generating the lattice, let us call the shorter one $\vec{a}_{\parallel}^*$ and the other $\vec{b}_{\parallel}^*$. Subtract $\vec{a}_{\parallel}^*$ from $\vec{b}_{\parallel}^*$ to obtain a new vector $\vec{b}_{\parallel}^*$. If the new vector $\vec{b}_{\parallel}^*$ is shorter, repeat. If $\vec{b}_{\parallel}^*$ ends up being shorter than $\vec{a}_{\parallel}^*$, exchange their roles. Eventually the length of the $\vec{b}_{\parallel}^*$ vector cannot be reduced any further and the “best” base $\vec{a}_{\parallel}^*, \vec{b}_{\parallel}^*$ is found. Gauss proved that this will always be achieved in a finite number of steps; in fact, the algorithm is quite efficient.

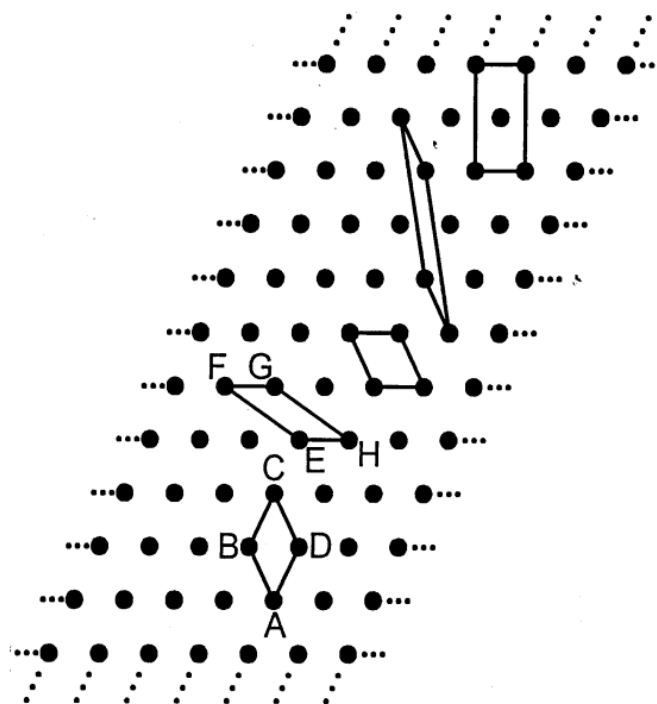


Figure 1. Unit cells of very different shapes can produce the same 2D lattice. The first four unit cells from left to right are primitive unit cells and the right-most cell is the unit cell of the centered rectangular lattice with two lattice points per unit cell, which best reflects the symmetry of the shown lattice. The task of crystallography is to specify rules for a unique “best” unit cell. This cell is defined by the requirement that two lattice vectors be chosen with the shortest length and an enclosed angle as close to 90° as possible. This would be the cell in the center and these are the cells we will be concerned with in the following. Republished from Ref. [28] courtesy of the National Institute of Standards and Technology.

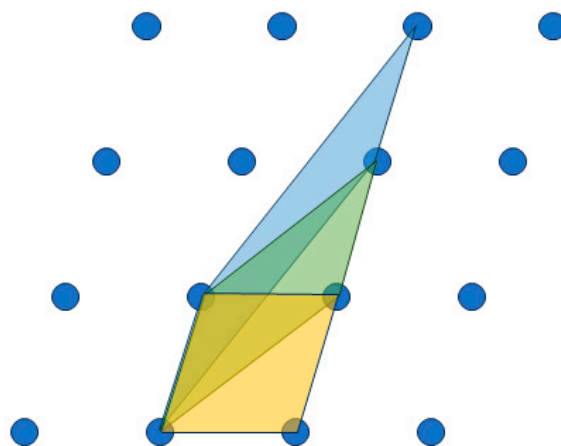


Figure 2. Lagrange–Gauss reduction to find the “best” unit cell for a 2D lattice which is given by the shortest two lattice vectors with an enclosed angle close to 90° . Shown here is an arbitrary unit cell (blue) being reduced in two steps (green and orange) to the “best” unit cell (orange) using the Lagrange–Gauss algorithm.

This lattice reduction algorithm provides a finite scheme to obtain a unit cell with the two shortest possible lattice vectors $\vec{a}_\parallel^*$ and $\vec{b}_\parallel^*$ with lengths $a_\parallel^* \leq b_\parallel^*$ and an enclosed angle $\gamma_\parallel^*$ close to 90° . In fact, from the algorithm, it follows directly [29,30] that

$$60^\circ \leq \gamma_\parallel^* \leq 120^\circ \quad (3)$$

where the equality is assumed for the hexagonal lattice with $a_\parallel^* = b_\parallel^*$.

Independent of specific unit cell choices, two 2D lattices are identical if there is a combination of rotations and translations that maps the lattice points onto each other. If we are only interested in the *lengths* of lattice vectors, as in our further analysis, two such lattices can be said to be equivalent when they can be brought to match if also a mirror reflection is involved. This is the case for any angle $0 < \theta < 30^\circ$ and lattices that have the same $a_\parallel^*$ and $b_\parallel^*$ but $\gamma_\parallel^* = 90^\circ + \theta$ and $\gamma_\parallel^* = 90^\circ - \theta$. Thus the range of $\gamma_\parallel^*$ for equivalent lattices can be further reduced to

$$60^\circ \leq \gamma_\parallel^* \leq 90^\circ \quad (4)$$

Here we chose to have an acute angle between $\vec{a}_\parallel^*$ and $\vec{b}_\parallel^*$. This choice is consistent with the use of obtuse angles in real space and acute angles in reciprocal space in crystallography. Lagrange–Gauss reduction considerably reduces the available parameter space for the lattice parameters and also provides a unique parameter set, which has further important properties.

For a unit cell spanned by vectors $\vec{a}_\parallel^*$ and $\vec{b}_\parallel^*$, we obtain the lengths of the diagonals:

$$d_\parallel^* = q(-1, 1) = \left| \vec{b}_\parallel^* - \vec{a}_\parallel^* \right| = \sqrt{a_\parallel^{*2} + b_\parallel^{*2} - 2a_\parallel^* b_\parallel^* \cos(\gamma_\parallel^*)} \quad (5a)$$

$$d_\parallel^* = q(1, 1) = \left| \vec{a}_\parallel^* + \vec{b}_\parallel^* \right| = \sqrt{a_\parallel^{*2} + b_\parallel^{*2} + 2a_\parallel^* b_\parallel^* \cos(\gamma_\parallel^*)} \quad (5b)$$

With the choice of $\gamma_\parallel^*$ to be acute and, hence, $\cos(\gamma_\parallel^*) > 0$, $d_\parallel^*$ is the shorter diagonal (see Figure 3). Moreover, $d_\parallel^*$ is also the third shortest lattice vector with $b_\parallel^* \leq d_\parallel^* \leq d_\parallel^* < 2b_\parallel^*$, except for colinear multiples of $\vec{a}_\parallel^*$, which will be ignored. All in all, we obtain an alternative way to uniquely describe the lattice by the set of vectors of shortest lengths $a_\parallel^*$, $b_\parallel^*$, $d_\parallel^*$ that

are not pairwise colinear. This is due to the fact that a triangle is uniquely given by two sides and the enclosed angle or, alternatively, by three sides (see Figure 3). The importance of the cell diagonal was realized in the classic works of Selling and Delaunay as well as Niggli in their efforts to determine a uniquely defined unit cell in three dimensions [31–33].

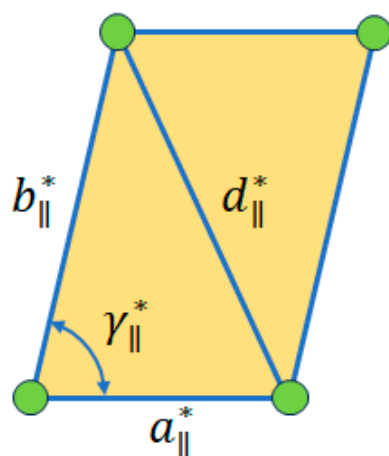


Figure 3. The reduced unit cell is given by sides $a_{||}^*$, $b_{||}^*$ and enclosed acute angle $\gamma_{||}^*$. Alternatively the cell is given by the triangle with sides $a_{||}^*$, $b_{||}^*$ and the cell diagonal $d_{||}^*$. For a unit cell obtained with Lagrange–Gauss reduction with $60^\circ \leq \gamma_{||}^* \leq 90^\circ$, $d_{||}^*$ fulfills the condition $b_{||}^* \leq d_{||}^* \leq d_{||}^* < 2b_{||}^*$ and has thus the third shortest lattice vector length, except for possible multiples of $a_{||}^*$, which need to be disregarded in the further analysis.

3.4. The Indexing Problem

The latter description of the reduced unit cell is well suited to tackle the indexing problem for the 2D lattice of the parallel components. From the analysis of a GIWAXS image, a series of q -values can be derived with

$$q_1 < q_2 < q_3 < \dots \quad (6)$$

If we can assume that we have observed a complete set of q -values and considering the properties of the “best” unit cell, we can identify the first q -values in this sorted set with $a_{||}^*$, $b_{||}^*$, and d if we carefully include special cases:

Case 1: Hexagonal lattice

$$a_{||}^* = b_{||}^* = d_{||}^* = q_1 : \gamma_{||}^* = 60^\circ \quad (7)$$

Case 2: Rhombic lattice (including square)

$$a_{||}^* = b_{||}^* = q_1, d_{||}^* = q_2 : \gamma_{||}^* = \arccos\left(\left(2a_{||}^{*2} - d_{||}^{*2}\right)/2a_{||}^{*2}\right) \quad (8)$$

Case 3: Oblique lattice (including rectangular)

$$a_{||}^* = q_1, b_{||}^* = q_2, d_{||}^* = q_3 : \gamma_{||}^* = \arccos\left(\left(a_{||}^{*2} + b_{||}^{*2} - d_{||}^{*2}\right)/2a_{||}^* b_{||}^*\right) \quad (9)$$

From the best match of these three cases, we can calculate $q(h, k)$ for a suitable range of h and k and then sort them by length and compare this sequence with the experimentally obtained sequence. This approach avoids guessing of indices h, k but instead relies on sorting q_i by length, which will also be of importance for the further refinement step. Figure 4 illustrates how the scattering rods determined by the three possible cases compare and it can be clearly seen that Case 3 is the correct choice in this example. Figure 4 was generated using the reciprocal space mode of program *indexGIXS* (Version 2T) [34]. The

test data set was obtained from a thin film of the conjugated molecule TES-ADT (5,11-bis (triethyl silylethynyl) anthradithiophene) [35]. For details see the Supplementary Materials.

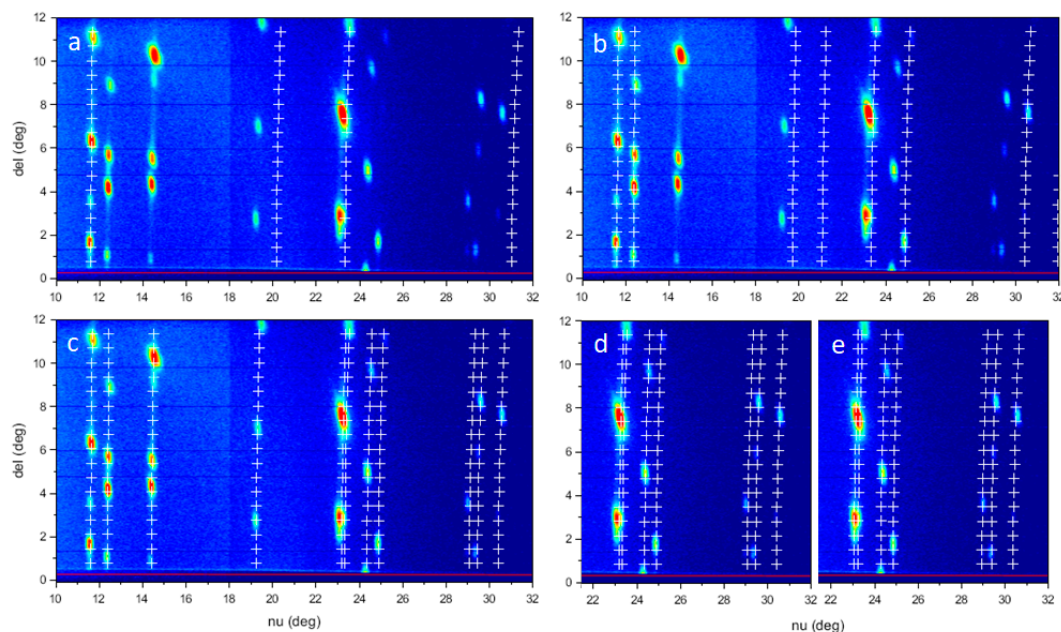


Figure 4. Calculation of the scattering rods of a TES-ADT film for the three cases of possible assignments of a^* , b^* , d^* with the measured scattering data (a–c). Panels (d,e) compare the matching of higher-order scattering rods before and after least-squares refinement.

3.5. Further Refinement

After having established a good starting point, the lattice constants can be refined further. Since we only made use of the first three q_i for the starting point at most, we have to take into account that small experimental errors remain, which can affect the match for the higher q_i , in particular for triclinic lattices. Hence it is desirable to include all observed q_i in the refinement, in order to improve the overall match and make full use of the available information. The next task is to relate the calculated spots with the measured sequence. It is important for this step to identify possible overlapping spots or spots that are too weak to be observed. Below, in Table 1, the matching of calculated and experimental data is illustrated based on the example shown in Figure 4.

Table 1. Sorted q -values and their Miller indices h, k based on the initial starting point and matched up with q -values from the observed sequence.

h	k	q_i^{calc}	q_i^{exp}
1	0	8.82	8.82 *
0	1	9.40	9.40 *
1	1	10.95	10.95 *
1	−1	14.57	14.5
2	1	17.52	17.45 **
2	0	17.64	17.45 **
1	2	18.40	18.33
0	2	18.80	18.75
2	2	21.9	21.8
2	−1	22.18	22.1
1	−2	22.89	22.9

* The initial assignment. ** Closely spaced calculated q vectors get assigned the same experimentally determined q -value assuming spots were closely spaced and not resolved, as judged by the scattering pattern and calculated values. In a case where q -values should have been resolved but no spot was observed, the q -value is eliminated from the refinement.

Using this table we now have a system of equations that can be linearized:

$$q_{exp}^2(h, k) = h^2 X + k^2 Y + hk Z \quad (10)$$

with

$$X = a_{\parallel}^{*2}, Y = b_{\parallel}^{*2}, Z = 2 a_{\parallel}^* b_{\parallel}^* \cos(\gamma_{\parallel}^*) \quad (11)$$

by rewriting Equation (2). This system of equations is overdetermined, but a least-squares optimization can be performed. We construct the matrix M with columns h^2 , k^2 , and hk for all q_i :

$$M = \begin{pmatrix} h^2 & k^2 & hk \end{pmatrix}. \quad (12)$$

The equation system can be written then as

$$M \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} q_{exp}^2 \end{pmatrix}. \quad (13)$$

The least-squares problem leads to the normal equations:

$$M^T M \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = M^T \begin{pmatrix} q_{exp}^2 \end{pmatrix}, \quad (14)$$

and its solution X, Y, Z yields the refined reciprocal lattice constants:

$$a_{\parallel}^* = \sqrt{X}, b_{\parallel}^* = \sqrt{Y}, \gamma_{\parallel}^* = \arccos(Z / 2 a_{\parallel}^* b_{\parallel}^*) \quad (15)$$

For TES-ADT we found the following lattice parameters for the in-plane components of the reciprocal surface unit cell: $a_{\parallel}^* = 8.76 \text{ nm}^{-1}$, $b_{\parallel}^* = 9.39 \text{ nm}^{-1}$, and $\gamma_{\parallel}^* = 73.66^\circ$.

3.6. Reconstructing the 3D Surface Unit Cell

When the 2D lattice of the parallel lattice vector components has been found, it is straightforward to obtain the perpendicular components. If the data set covers the $(00l)$ scattering rod, c^* can be determined directly from the $q_{\perp}$ -value of the lowest diffraction spot along the scattering rod. Similarly $a_{\perp}^*$ and $b_{\perp}^*$ can be directly obtained from the $(10l)$ and $(01l)$ scattering rods, respectively, by determining the position of the diffraction spots with the lowest perpendicular components (see Figure 5). If $(00l)$ is not part of the data set, c^* can be obtained by matching the spacing of the diffraction spots on the two special scattering rods. Then a similar refinement as outlined in Section 3.5 can be performed, now for the full 3D lattice associated with the reciprocal surface unit cell [5]. With this information the 3D lattice vectors of the reciprocal surface unit cell can be reconstructed

$$\vec{a}^* = \begin{pmatrix} a_{\parallel}^* \\ 0 \\ a_{\perp}^* \end{pmatrix}, \vec{b}^* = \begin{pmatrix} b_{\parallel}^* \cos(\gamma_{\parallel}^*) \\ b_{\parallel}^* \sin(\gamma_{\parallel}^*) \\ b_{\perp}^* \end{pmatrix}, \vec{c}^* = \begin{pmatrix} 0 \\ 0 \\ c^* \end{pmatrix} \quad (16)$$

and then back-transformed to the more familiar real-space surface unit cell.

Finally the standard lattice parameters are obtained as the lengths of the lattice vectors and the angles between the lattice vectors [5]. As for the example shown in Figure 4, the thin-film surface unit cell for triclinic TES-ADT was found to have the lattice parameters $a = 0.70 \text{ nm}$, $b = 0.75 \text{ nm}$, $c = 1.76 \text{ nm}$, $\alpha = 96.6^\circ$, $\beta = 92.3^\circ$, and $\gamma = 106.0^\circ$, slightly

distorted from the bulk unit cell parameters $a = 0.67$ nm, $b = 0.73$ nm, $c = 1.67$ nm, $\alpha = 98.1^\circ$, $\beta = 94.5^\circ$, and $\gamma = 103.9^\circ$.

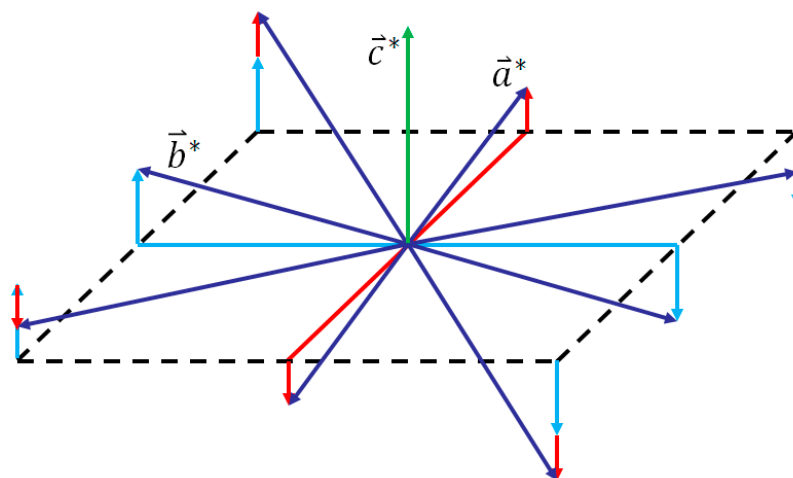


Figure 5. Reciprocal lattice vectors and their parallel and perpendicular components for a triclinic single crystal. For a 2D powder all reflections are averaged by rotation around the $\vec{c}^*$ axis. When $\vec{a}_\parallel^*$ and $\vec{b}_\parallel^*$ have been identified, the perpendicular components can be directly obtained from the scattering image. Reproduced from [5] with modifications.

3.7. Forbidden Scattering Rods

For monoclinic lattices with the common space group $p2_1/a$, the whole $(10l)$ scattering rod is forbidden when (001) is the texture plane parallel to the surface. Note that this is a rather restrictive condition; it only occurs for glide planes and only for a specific orientation of the molecular planes so that the glide translation vector lies in the molecular plane. Nonetheless this situation is not uncommon; for instance, polymorphs of anthracene, pyrene, and perylene assume such thin-film structures [5].

The whole $(10l)$ scattering rod being forbidden means that we have to assign q_1 as $b_\parallel^*$ and q_2 as $d_\parallel^*$. Next we have to consider all higher q_i with $i \geq 3$, for which $q_i/2 < d_\parallel^*$, and then tentatively assign $a_\parallel^*$ to be $q_i/2$. We should find a promising match of experimental and calculated q_i in a finite number of trials. This process is illustrated in Table 2 for the case of C8-BTBT (2,7-dioctyl [1]benzothieno [3,2-b][1]benzothiophene), a conjugated molecule with excellent charge mobility [36]. Figure 6 shows a typical GIWAXS pattern for a thin film of C8-BTBT deposited on a silicon wafer, which could be indexed following this procedure. The streak-like shape on the diffraction spots is due to the small sample-detector distance compared to the width of the sample [37]. For details see the Supplementary Materials.

It is straightforward to generate the trial assignments for $a_\parallel^*$ using Equation (2) and see also the Supplementary Materials. Correlation with the measured values takes some careful reasoning with regard to resolution and to identify unobserved reflections. Nonetheless, it becomes quickly clear that only choice of q_5 provides an overall good match with q_{exp} . Following the procedure outlined in Sections 3.5 and 3.6 the thin-film lattice of C8-BTBT was found to be identical to the bulk structure [36] with lattice parameters $a = 0.593$ nm, $b = 0.788$ nm, $c = 2.918$ nm, and $\beta = 92.4^\circ$.

We note that this procedure can also be applied to molecule lattices with space group $p2_1/c$ and a (100) growth plane by transforming the lattice to yield space group $p2_1/a$ [24]. Space group $p2_1/a$ was highlighted here, because it fits in a natural way with the conventions of the surface unit cell. This scheme can also be employed in case there is reason to believe that one of the first three scattering rods is too weak to be observed.

Table 2. Identification of lattice parameter $a_{\parallel}^*$ for a monoclinic unit cell with a glide plane that renders the $(10l)$ rod forbidden. The headers indicate which q_i was tested to be a candidate for $2 a_{\parallel}^* = q(2, 0)$.

$a_{\parallel}^*=q_3/2$	$a_{\parallel}^*=q_4/2$	$a_{\parallel}^*=q_5/2$	$a_{\parallel}^*=q_6/2$	$a_{\parallel}^*=q_7/2$	q_{exp}
8.00	8.00	8.0	8.00	8.00	8.0
8.00	9.60	10.65	11.40	8.10	— *
8.89	11.64	13.3	13.30	9.07	13.30 **
13.30	13.30	13.34	14.53	13.30	13.30
14.91	16.00	16	16.00	15.07	16.00
14.91	17.51	19.19	18.76	15.03	19.2
16.00	19.20	19.26	20.50	16.00	19.2
16.00	19.74	21.30	22.80	16.20	21.30
17.79	19.78	22.73	23.45	18.15	(22.80) ***
20.44	21.77	22.78	24.00	20.40	(22.80) ***
20.44	23.27	12.00	24.86	20.57	— ****
22.21	24.00	26.23	25.59	22.36	26.2
22.21	24.62	26.29	26.60	29.36	26.2

* Forbidden by glide plane, ** assigned as d , *** very weak reflections, **** not observed—too weak.

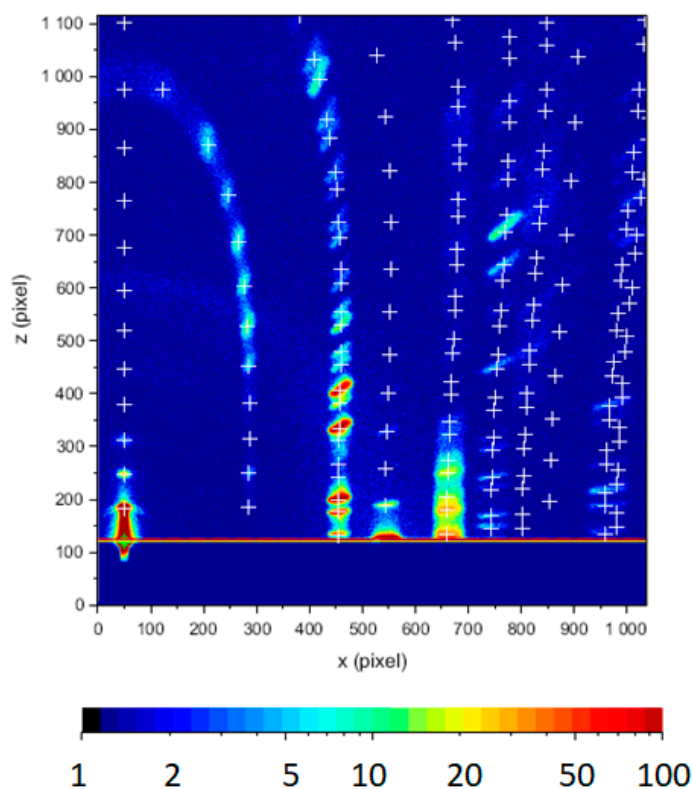


Figure 6. Grazing-incidence scattering pattern of a C8-BTBT film. The markers trace the scattering rods of the q_i identified with the procedure explained in the text and in Table 2. Note that the important q_1 value was obtained thanks to diffraction spots along the $(10l)$ rod at high $q_{\perp}$ values.

Finally we note that space-group forbidden scattering rods can also occur in the orthorhombic system when the low-index molecular planes (100) , (010) , or (001) are formed parallel to the substrate surface. According to the current statistics of the Cambridge Structural Database, only 5.5% of known molecular structures have a higher symmetry, while triclinic (26.2%) and monoclinic structures (51.4%) are the most common [38].

3.8. Multiples of $a_{\parallel}^*$

Multiples of $a_{\parallel}^*$ can be a problem when $a_{\parallel}^*$ is much smaller than $b_{\parallel}^*$, i.e., when $2 a_{\parallel}^*$ and so forth are smaller than $b_{\parallel}^*$ or $d_{\parallel}^*$. However, such q -values can be easily identified and

skipped over when assigning $b_{\parallel}^*$ and $d_{\parallel}^*$. Another issue to consider here is that $b_{\parallel}^*$ and $d_{\parallel}^*$ will be very close and may not be resolved, i.e., $b_{\parallel}^* \approx d_{\parallel}^*$ (see Figure 7). Equation (9) can be rewritten in this case as

$$a_{\parallel}^* = q_1, b_{\parallel}^* = d_{\parallel}^* = q_2, \gamma_{\parallel}^* = \arccos(a_{\parallel}^*/2 b_{\parallel}^*) \quad (17)$$

which can be considered as Case 4. Otherwise the analysis can proceed the same way as in Case 3.

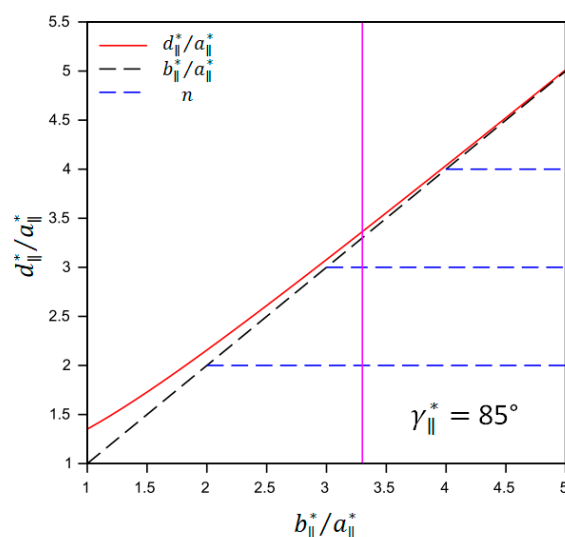


Figure 7. Separation of $d_{\parallel}^*$ (red solid line) and $b_{\parallel}^*$ (black dashed line) as a function of $b_{\parallel}^*/a_{\parallel}^*$ for $\gamma_{\parallel}^* = 85^\circ$. Multiplies of $a_{\parallel}^*$ are indicated as the horizontal dashed blue lines. The vertical purple line indicates the expected sequence of q -values for a specific value of $b_{\parallel}^*/a_{\parallel}^*$.

In such a case it should also be checked whether q_1 is not $a_{\parallel}^*$ but actually $2 a_{\parallel}^*$, i.e., if the lattice is monoclinic with a forbidden scattering rod. If a match is still not successful, it should also be checked whether $b_{\parallel}^*$ accidentally coincides with a multiple of $a_{\parallel}^*$ by constructing a similar table as Table 2.

3.9. Other Complications

Finally there can be additional reflections from either the substrate, another film polymorph, and some other impurity in the film. First thing to look for is whether there is a difference in the radial and tangential spot widths or the overall spot shape in order to identify such interlopers and remove them from consideration. Other than that, there would be multiple trials needed, with various combinations of spots taken out of consideration. In such a situation recent computational methods may be a better option [39–42]. This case is the worse case scenario for any kind of indexing approach but, fortunately, the likelihood that such a q -value would be among the first three q -values of the film is finite.

4. Conclusions

A systematic approach to indexing 2D powders is presented that makes use of results based on classic mathematical work by Lagrange and Gauss. The reduced reciprocal unit cell of a thin film has important properties; in particular, it establishes that the shortest in-plane q -vectors can be identified with $a_{\parallel}^* = q(1, 0)$, $b_{\parallel}^* = q(0, 1)$, and $d_{\parallel}^* = q(1, -1)$. The method is particularly useful for primitive lattices of triclinic and monoclinic symmetry, which are formed by the vast majority of small molecules. Crystallographers have tackled such problems for 3D powder diffraction and found similar lattice reduction schemes in 3D, resulting in the modern convention for assigning bulk unit cells [43]. The case of 2D

powders lies somewhere in between pure 2D and 3D systems, with the six lattice constants of highly textured molecular thin films separating into 3 + 3 parameters for the surface unit cell in reciprocal space. Making use of complete scattering rods to identify the in-plane q_i should help to overcome the problem of missing reflections. For space-group forbidden scattering rods, a way to recover the missing q -value has been discussed.

The approach has been successfully applied to indexing triclinic and monoclinic lattices in organic semiconductors. While the focus here was on low-symmetry lattices, we note that the approach does not preclude application to lattices with higher symmetry. However, there are more extended glide-plane symmetries, in particular for the orthorhombic system, which can lead to more missing scattering rods. Such lattices are much less common for small molecules, though, and hence the presented approach should cover a large variety of molecular thin films. Although not exhaustively complete, the outlined approach provides a good starting point to find an indexation for the reciprocal surface unit cell from which the 3D surface unit cell in real space can then be obtained.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst16010043/s1>, Experimental parameters for Figures 4 and 6; Programing notes for Tables 1 and 2 and the refinement procedure.

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Data Availability Statement: Software and data sets used in this work can be obtained from the author upon reasonable request. Key data are listed in Tables 1 and 2. Sample preparation and data acquisition as well as the scripts to generate Tables 1 and 2 are listed in the Supplementary Materials.

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Abbreviations

The following abbreviations are used in this manuscript:

GISAXS	Grazing-incidence small-angle X-ray scattering
GIWAXS	Grazing-incidence wide-angle X-ray scattering
TES-ADT	5,11-bis (triethyl silylethynyl) anthradithiophene
C8-BTBT	2,7-dioctyl [1]benzothieno [3,2-b][1]benzothiophene

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