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ORIGINAL PAPER

Modelling of X-ray patterns using Fourier transforms: application to nanomaterials

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Abstract: Stucture of crystalline materials is obtained by studying the diffraction patterns using electromagnetic radiations like X-rays, electron and neutron beams. These patterns are essentially Fourier transforms of the sample space. As the diffraction pattern corresponds to reciprocal lattice of the atomic arrangement, Fourier transform can be used to convert the data from real space to reciprocal space. Thus, an image of real space when transformed to Fourier space should resemble the X-ray diffraction profile. For this, we have developed an algorithm for image processing using Fourier transform employing GNU Octave. In essence we would like to investigate the Fourier transform of several two-dimensional ordered systems which mimic two dimensional nanostructures in general. For this, we have built several two-dimensional models to study the ordered patterns with various shapes of the repeating entity like circular, rectangle, squares, benzene shape along irregular patterns. We study the variation in diffraction patterns that are in transformed space and compare them inorder to simulate with two dimensional images.

Keywords: Fourier transform; Microstructure; Two-dimensional modeling; XRD

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1. Introduction

For X-rays interacting with the sample (which is crystalline), we have Bragg equation given by $n\lambda = 2d\sin\theta$, where λ is the wavelength of X-rays used, d is the lattice spacing and Θ is the Bragg angle. Using this equation along with Laue symmetry associated with the crystal or the sample; the cell dimensions, bond lengths, bond angles and thereby crystal structure can be determined. There are various computation procedures including Rietveld method to obtain the structure solutions from the X-ray powder data. Crystal structure can also be obtained from single crystal X-ray data and by using SHELEX crystal structure software. Most of the scattered X-ray or diffracted data lies in reciprocal space or Fourier transformed space. For almost 5 decades, the study of broadening of X-ray Bragg reflections has been on the forefront. Recently, these methods have been validated using microbeam diffraction from individual dislocation cell walls and cell interiors [1]. There is a continued interest in arriving at a suitable reliable method to compute the microcrystalline parameters using different techniques. In 1918 Scherrer proposed a method [2] to compute crystallite size based on the shape of the intensity profile. Warren and Averbach [3] gave Fourier analysis technique to compute crystallite size and lattice strain, whenever two orders of reflections are available. Scardi and Leoni [4] introduced whole powder pattern modelling method (WPPM) to compute microstructural parameters, which eventually turned-out to be the most accepted approach. Besides the fact of it being questioned, for the truncation of profile range and assumption of crystallite size as isotropic in nature.

In this continued journey of understanding the phenomena and basics of crystal structure, we are defining a

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new aspect of structure modelling using Fourier transforms. Keeping in mind that, the diffraction is the Fourier transformed image of the real space, we transform regular two dimensional image representing structure, in order to verify the transformed results. We develop an algorithm for image processing using Fourier transform employing GNU Octave [5], to investigate the Fourier transform of several two-dimensional ordered systems which mimic two dimensional nano materials. The variation in diffraction patterns, which is in transformed space is studied and compared with the reported data. A comparison of experimental data reported for several two-dimensional nano systems with simulated patterns using the method described here has been made. We have built several two-dimensional models to study the ordered patterns with various shapes of repeating entities like circular, rectangle, squares, benzene shape and irregular patterns. We have also made an attempt to study the effects of defects in these ordered systems on the diffraction patterns.

1.1. Reciprocal basis in two dimensions

In two dimensions, i.e., a plane, we have two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ that are not parallel or antiparallel to each other. We need to find two other vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ in the same plane so that, $\boldsymbol{A}.\boldsymbol{a} = \boldsymbol{B}.\boldsymbol{b} = 1$; while, $\boldsymbol{A}.\boldsymbol{b} = \boldsymbol{B}.\boldsymbol{a} = 0$ [6]. The two-dimensional analogue of the volume V of the parallelepiped is the area $\boldsymbol{a}\times\boldsymbol{b}$ of the parallelogram formed by ($\boldsymbol{a}$, $\boldsymbol{b}$). Then the area V is given by, $V^2 = a^2b^2 - (\boldsymbol{a}.\boldsymbol{b})^2$ where, $\boldsymbol{a}^2 = \boldsymbol{a}.\boldsymbol{a}$ and $\boldsymbol{b}^2 = \boldsymbol{b}.\boldsymbol{b}$.

The cross product of two vectors in two-dimensional space gives us only one component instead of two to make a two-dimensional vector. We can write the area in the form of the determinant formed by writing out the basis vectors in component form in two dimensions, one after the other, i.e.,

$$\begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} \tag{1}$$

Using the Levi-Cevita symbol, we can write (in two-dimensions),

$$V = \boldsymbol{a} \times \boldsymbol{b} = a_1b_2 - a_2b_1 = \sum_{i=1}^{2}\sum_{j=1}^{2} \epsilon_{ij}a_ib_j \tag{2}$$

where

$$\epsilon_{ijk\ldots} = \begin{cases} +1 & \text{if } ijk\ldots \text{is an even permutation of the natural order} 123\ldots n; \\ -1 & \text{if } ijk\ldots \text{is an odd permutation of the natural order} 123\ldots n; \\ 0 & \text{whenever any two indices are equal.} \end{cases}$$

We now have all the pre-requisites that are needed to find the reciprocal basis in two-dimensions.

2. Modelling

To study the ordered patterns with various shapes of the repeating entity like circle, rectangle, square benzene shape, irregular patterns and several two-dimensional models have been built using the Xfig application. An attempt has also been made to study the effect of defects in these ordered systems on diffraction patterns. The distance (a) between the centres of the adjacent repeating units in the 2-dimensional lattice was noted, and then the distance (b) of the first peak from the centre in the reciprocal space was calculated. Finally the conversion factor required to compute the real space two-dimensional cell parameter was determined.

2.1. Source code of GNU Octave program

```
clf;
clear all;
b = imread (\100.bmp");
c = cast (b,`int8');
[x,y,z]=size(c);
for k=1:x
for l=1:y
if (c(k,l) >100)
c(k,l) = 1;
else
c(k,l) = 0;
endif
endfor
endfor
a = _tshift(_t2(c(:,:,1)));
z = abs(a);
surf(1:y,1:x,z,`edgecolor',`none')
contour(1:y,1:x,z,`edgecolor',`none')
plot(1:x,z)
plot(1:y,z)
```

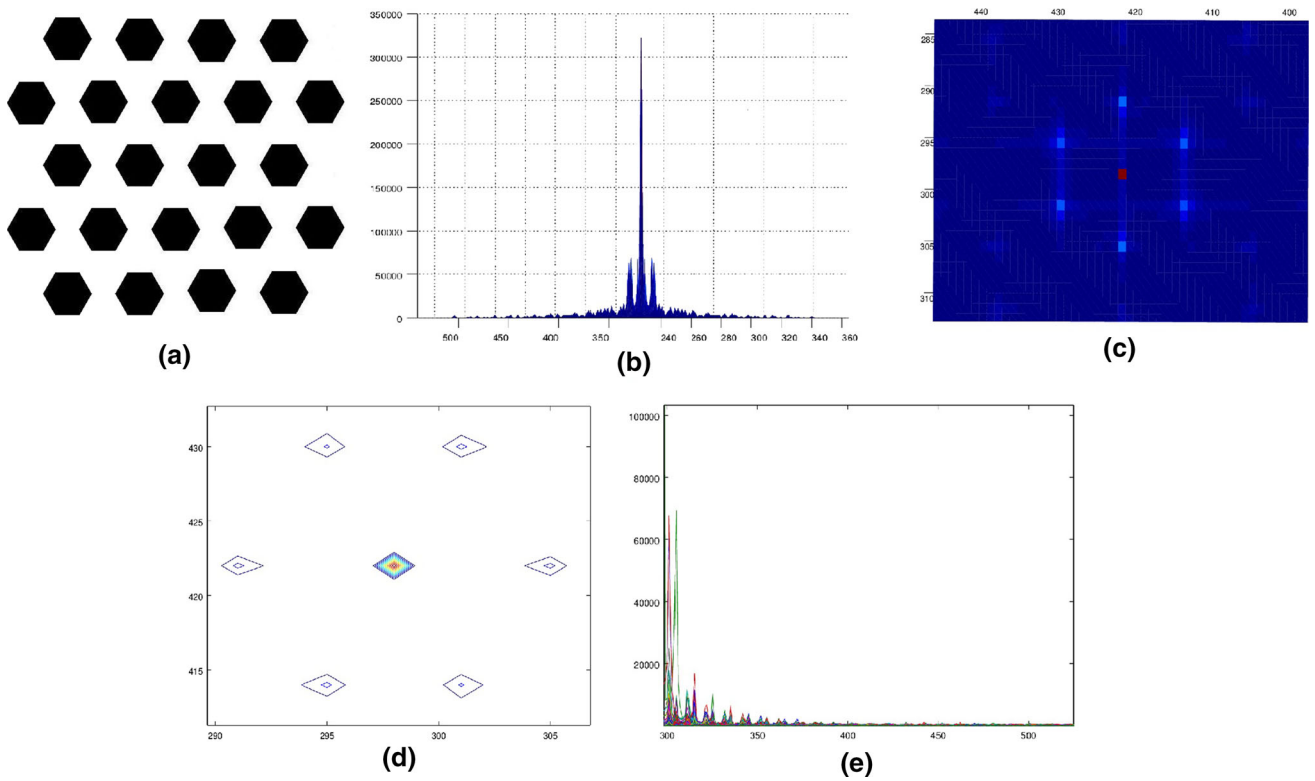


Fig. 1 Hexagonal pattern and its Fourier transforms—(**a**) lattice in real space, (**b**) surface plot, (**c**) sample space image, (**d**) contour plot and (**e**) (y, z) plot

2.1.1. GNU Octave

The Octave function provides a two-dimensional plot. Depending on whether the plot in discussion is the (x; z) or the (y; z) plot, it gives the corresponding distance between the peaks, which in turn gives us the distance between the points in the reciprocal space. However, when an equation or any function is a scalar quantity that depends on two variables, the two-dimensional plot does not come in handy. In such conditions, a three dimensional view to relate the two variables with the function is required. The graph of this function can be visualized via a surface plot which can be obtained by using the Octave function 'surf'. This surface plot, when rotated using the mouse controls, gives an outline of the sample space image that we have created using Xfig. Sometimes, the three dimensional view of the surface plot makes it difficult to view fine details, in such a case contour plot helps. Octave based contour helps in obtaining the contours of the required functions. The distance between the centres of the adjacent contours taken either in the equatorial line or the axial line gives us the distance between the points in the reciprocal space [7].

2.2. Xfig

In LINUX, XFig is one of the most popular and widely used programs to produce diagrams. XFig is a vector drawing program, and it has a few paint-program features. Vector drawing programs work with drawing elements such as lines, circles and polygons. These elements may be grouped and manipulated in various ways, such as being moved or sized. These Vector drawing programs are well suited for technical work such as electronic schematics and mechanical diagrams. Whereas, images drawn in jpg format will be in pixels which makes it difficult to determine the distance [8].

2.3. Two-dimensional Xfig images

The following two dimensional images were created using the Xfig application. The images are scaled in centimeters. The Fourier transformed images of the two-dimensional ordered patterns have been obtained by executing the above octave program.

2.3.1. Perfect lattices

Crystal is a solid composed of atoms, ions or molecules that demonstrate long range periodic order in two or three dimensions. The structure which is repeated regularly in space is the motif and the conceptual array of points which define the geometrical relation between the motifs is the lattice. There are two particular features of lattice and motif

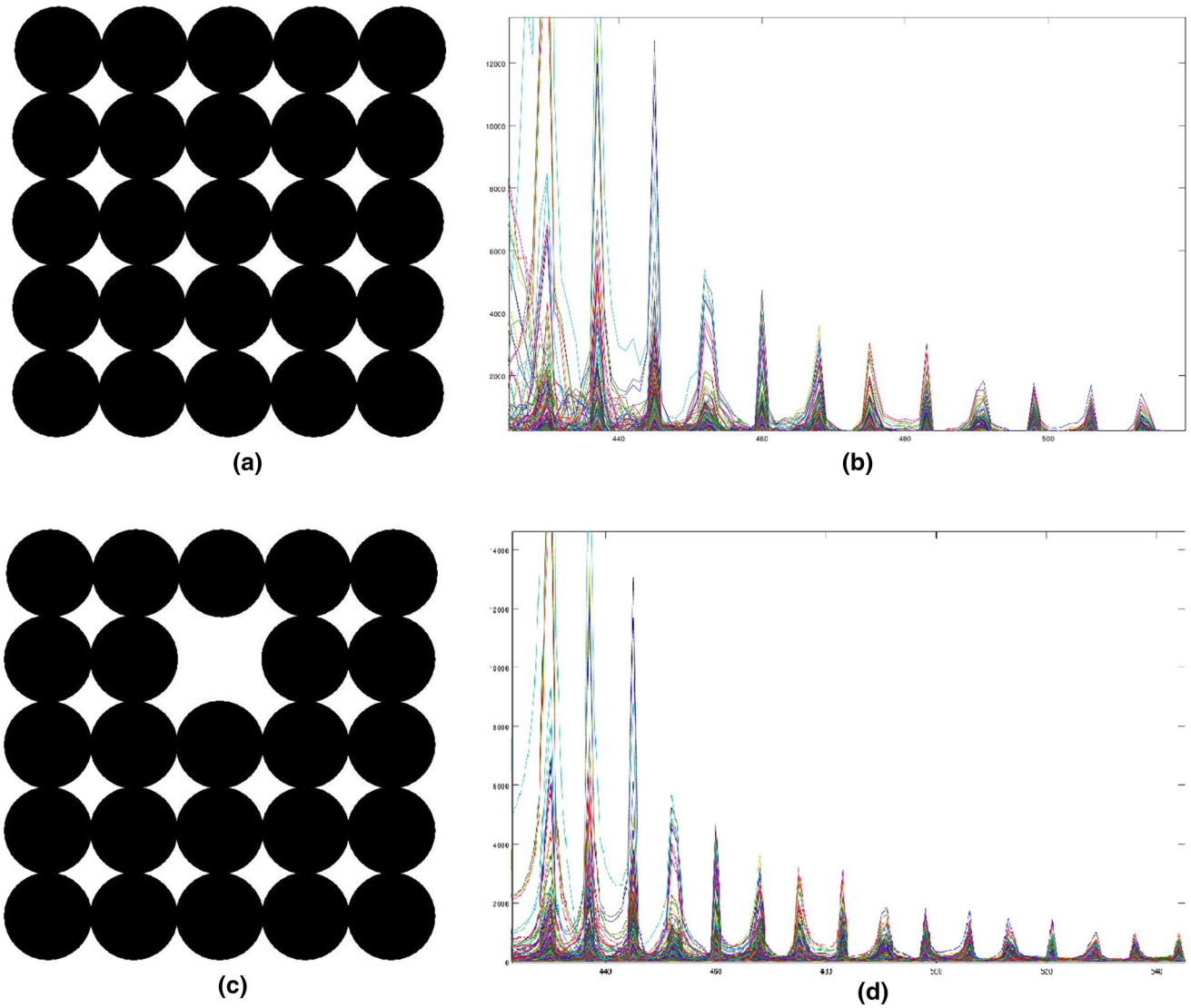


Fig. 2 Perfect monoatomic lattice (**a**) real space image, (**b**) corresponding (y, z) plot; (**c**) real space image of defect lattice and (**d**) corresponding (y, z) plot for vacancy defect

that are important: the position of lattice point with respect to motif is arbitrary, provided they are consistent and; the motif may be quite complex naturally.

In total, 13 perfect lattice two-dimensional images including the one shown above were been created in Xfig tool and their corresponding four plots (surface plot, contour plot, 2-dimensional plot) have been obtained using the GNU Octave program.

2.3.2. Lattices with defects

In total, 6 two-dimensional images have been created using Xfig tool and their corresponding four plots have been obtained using the GNU Octave program. And these plots of the imperfect lattice have been compared with the plots of the corresponding perfect lattice. It has been observed that the peaks in the two images appear at the same distance giving a constant conversion factor. But there is a spread in the diffraction pattern of the lattice with the defect, which is quite similar to X-ray diffraction whose profile gets broadened.

3. Results and discussions

The concept of this modelling was examined by various images generated as mentioned before, one of the two-dimensional models is considered for detailing. The hexagonal motif of a lattice in real space is Fourier transformed and its various views were captured in order to understand these transformations. Figure 1 shows various images like lattice in real space (Fig. 1a), surface plot (Fig. 1b), Contour plot

Table 1 Spatial distance and conversion factor of Xfig images

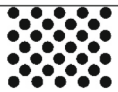
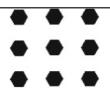
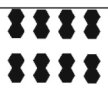
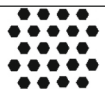
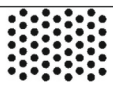
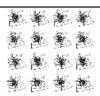
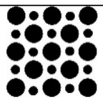
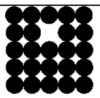
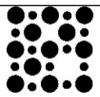
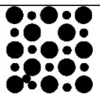
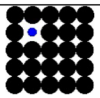
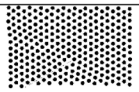
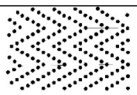
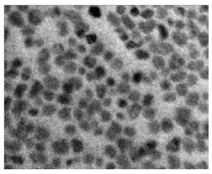
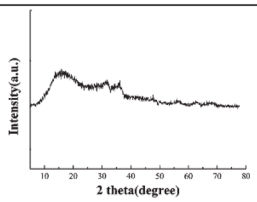
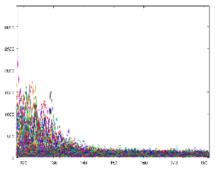
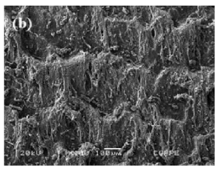
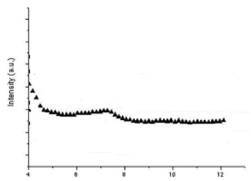
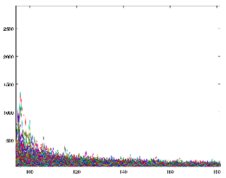
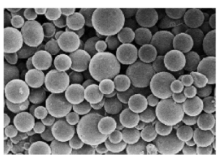
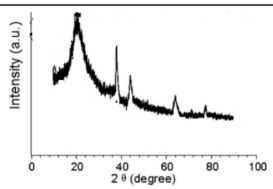
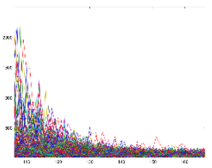
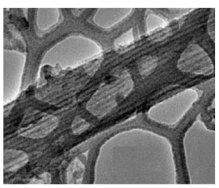
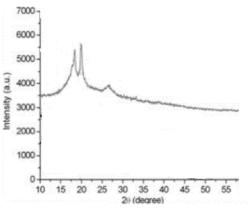
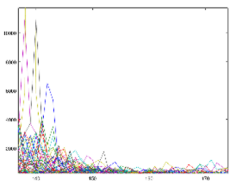
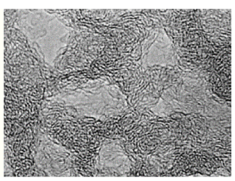
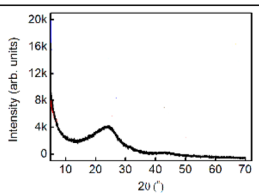
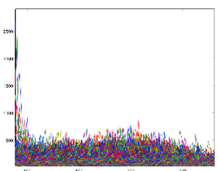
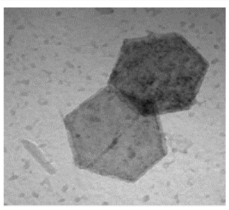
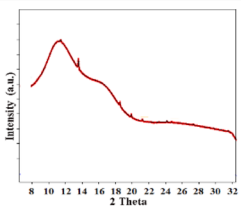
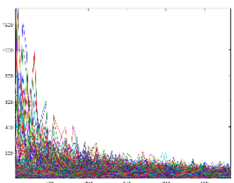
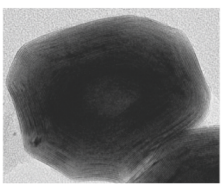
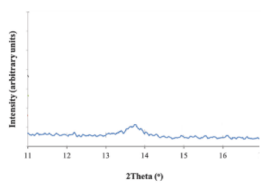
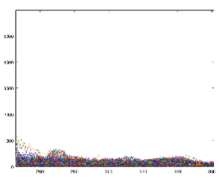
Image		Spatial distance		Conversion factor
		Real Space (*a*) in cm	Fourier Space (*b*) in cm	
Perfect Monoatomic Lattices				
Circle		4.0	0.132	0.528
Rhombus (Tilted Square)		2.8	0.185	0.518
Hexagon		2.0	0.264	0.528
Square (Chess Board) (FCC Lattice)		5.0	0.106	0.530
Rhombus		5.1	0.106	0.540
Triangle		5.0	0.106	0.530
Circle (FCC Lattice)		5.4	0.079	0.427
Hexagon		4.1	0.013	0.541
Hexagon (Naphthalene Molecule)		6.3	0.079	0.500
Hexagon (placed in the form of a hexagon)		6.1	0.079	0.482
Circle (placed in the form of a hexagon)		1.6	0.344	0.550
Irregular		3.0	0.187	0.560

Table 2 Spatial distance and conversion factor of Xfig images

Perfect Ionic Lattice				
Ionic Solid (NaCl, KCl)		4.0	0.132	0.528
Lattices with Defects				
Vacancy Point Defect		4.0	0.132	0.528
Schottky Defect		4.0	0.132	0.528
Frenkel Defect		4.0	0.132	0.528
Substitutional Point Defect		4.0	0.132	0.528
Edge Dislocation		1.6	0.344	0.550
Twin Boundary		1.6	0.344	0.550

$$\text{Mean Conversion Factor} = \frac{\text{Sum of the individual conversion factors}}{\text{Total number of images}} = \frac{9.92}{19} = 0.522$$

Table 3 Experimentally obtained X-ray diffraction patterns and corresponding observed plots of SEM Images

SEM image	Author	X-ray Diffraction Pattern given in the paper cited	X-ray Diffraction Pattern using the method described in this paper
	Ge et al. [9]		
	Mariano et al. [10]		
	An et al. [11]		
	Cauda et al. [12]		
	Zhang et al. [13]		
	Taglieri et al. [14]		
	Cook et al. [15]		

(Fig. 1c), sample space image (Fig. 1d) and the (y, z) plots (Fig. 1e). To study the effect of defects, a comparison of perfect lattice is made with the same lattice bearing a vacancy by considering (y, z) plot which almost resembles the 2θ versus intensity plot obtained from XRD. This is represented in Fig. 2, wherein Fig. 2(a, b) shows real space and (y, z) plots of perfect lattice; Fig. 2(c, d) gives real space and (y, z) plots of imperfect lattice. It can be seen that the peaks in the two images appear at the same distance giving a constant conversion factor. However, there is a spread in the diffraction pattern of the lattice with the defect, which is quite similar to the strain effects seen in materials, whose X-ray diffraction profile gets broadened. Similar tests were carried out for several such patterns and examined to verify our proposition, these were created using Xfig and the corresponding plots, contours in the reciprocal space were obtained (which are in Tables 1, 2). The relation between the spacing of the repeating units in the real space to the spacing between the central and the peak next to it in reciprocal space is noted. According to the theory of reciprocal space, this relation ought to provide unity, however, it does not. Interestingly, we have obtained a constant conversion factor for all the two-dimensional patterns which makes this possible. Tables 1 and 2, illustrate the patterns considered and their respective conversion factors. The distance of the repeating motifs in the real space and distance between the peaks in the reciprocal space are taken in centimeters. The constant conversion factor has been obtained from the Fourier transform of several two-dimensional ordered systems and these two-dimensional ordered systems mimic two-dimensional nanostructures. The Scanning and Transmission Electron Microscope (SEM and TEM) images and the corresponding X-ray diffraction patterns of a few nanomaterials have been collected from the already published papers for comparison. The ordering in nanomaterials is more disordered when compared to the ordering in small organic and inorganic molecules and hence, the resolution of the peaks in the Fourier transformed images is reduced to a large extent. The images of nanomaterials, the X-ray diffraction patterns reported in the papers cited and the pattern that we have obtained by executing the GNU Octave program is given in Table 3. These two plots (or patterns) are broadly in agreement with each other when we neglect the noise and consider only the envelop of the obtained pattern. The patterns given in the cited papers are a plot of intensity versus 2θ. The horizontal axis of our plot is scaled in pixels which can be converted to 2θ. The resemblance between the two plots makes it clear that, the calculation of the direct lattice spacing is possible by knowing the spacing of reciprocal lattice obtained through GNU Octave, along with the conversion factor which is calculated and with exact magnification factor of the images refered.

4. Conclusions

GNU Octave has been used to Fourier transform the sample space of the two-dimensional images which represents the X-ray diffraction pattern. The two-dimensional images generated using Xfig tool have a vector representation and the Fourier transform of such two-dimensional figures will have a one-to-one correspondence in all aspects including the spatial distance of images in the sample space or Fourier transformed space. Two-dimensional sample space images generated with image file extensions like .png, .jpeg, .eps do not have vector representation as such. Fourier transform of such images will have a one-to-one correspondence in all aspects except the spatial distance of images in the sample space or Fourier transformed space. It is always possible to generate sample space images corresponding to X-ray diffraction pattern using this technique, which is new and handy to correlate the sample property interior of sample space, and arrangements at atomic or molecular level. This technique has the added advantage of using enlarged images of samples, like SEM images and their Fourier transform which is an exact replica of X-ray diffraction pattern. This will aid in the better understanding of materials.

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