Chapter 3

Simulating Diffraction Patterns

3.1 Introduction

Diffraction techniques provide powerful tools to study how materials order at the atomic level. X-rays were first used to probe microscopic order, these have since been supplemented with electron and neutron scattering methods. In the specific case of this work the ordered structures produced by Monte-Carlo molecular dynamic simulations can be compared to real world samples by calculating their virtual diffraction patterns for comparison with those from experiment

The study of diffraction patterns from 3-d structures is very well established. Thomas Young famously observed two slit interference of light in ~1802 concluding that light was a wave rather than a particle as proposed by Newton - a debate that still continues to this day. Such interference patterns are a natural consequence of Huygens construction where every point on a waterfront may be assumed to be a source of secondary *wavelets*. 2-d diffraction gratings were well developed by the mid 1800s. The possibility of diffraction from 3-d atomic structures was suggested by Ewald and Laue in 1912 with the first x-ray diffraction pattern produced shorty thereafter.

The terminology here is somewhat imprecise. A diffraction pattern is the result of the *interference* of *diffracted* waves. At a physical level the processes are the same, we tend to use interference when referring to a few scatterers and diffraction for many.

X-rays, electrons and neutrons are used in atomic diffraction studies. Relatively inexpensive and compact equipment is capable of generating x-rays whose wavelength is of the order of the inter-atomic spacing. X-rays scatter from electrons thus the scattering power of an atom depends upon the number of electrons it possesses i.e. its atomic number. Palladium with 46 electrons scatters much more strongly Hydrogen with only 1. In the case of Pd-H, scattering from the palladium masks the signal from the hydrogen. Instead thermal neutrons with de-Broglie wavelengths of

the order of Å s may be used as the neutron scattering factor does not vary simply with Z number and is highest for hydrogen. A suitably bright neutron source may be a nuclear reactor, such as that at Grenoble or a proton synchrotron such as ISIS which generates neutrons by spallation from a tungsten target illuminated by protons. This equipment is many times larger, expensive and complex then x-ray diffractometers. As x-ray, electron and neutron scattering patterns are due to the summing of scattered waves from the target it is straightforward to simulate this process.

A brief overview of scattering theory is first presented followed by a discussion of how a diffraction pattern may be computed from a simulated sample.

3.1.1   General Scattering Theory

The kinematic model provides a simple view of scattering. An incident wave-front may be scattered by discontinuities in its path. X-rays scatter from orbital electrons whilst neutrons scatter from atomic nuclei. These scattering centres act as sources of spherical wavefronts (*s-wave* scattering). At some distance wave-fronts from many scatterers interfere thereby creating regions of high and low intensity depending on the phase contributions from each wave.
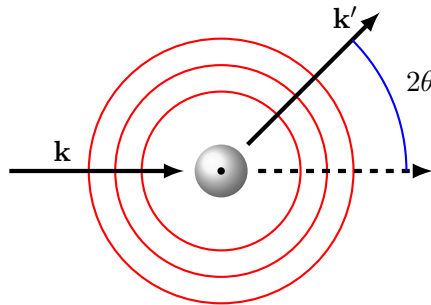

FIGURE 3.1: Simple Kinematic Scattering

In this simple treatment the scattering is assumed to be elastic i.e. the magnitude of the scattered wave vector is equal to that of the incident. $|\mathbf{k}'| = |\mathbf{k}|$. The amplitude of the incident wave arriving at a point j in the sample is given by $A_j = A_0 e^{i\mathbf{K} \cdot \mathbf{r}_j}$. Thus the scattered amplitude A_s arriving at a detector at a distance R_i from the ith atom is given by

$$A_i = \frac{A_0}{R_i} f e^{i(kx - \omega t)} \tag{3.1.1}$$

where f the scattering factor is a measure of the scattering power of the atom. If the distance to the detector is very much greater than the atomic spacing then R_i may be to a constant R. In reality a scattered wave is likely to undergo further scattering. In simple models this effect is ignored as it greatly increases computing time.

3.1.2 The Scattering Vector q

Consider two atoms i and j, illuminated by a coherent beam of radiation from a source at ∞, of wavelength λ and thus wavevector $|q| = \frac{2\pi}{\lambda}$. The difference between the incident and scattered wave vector is known as the scattering vector where $\mathbf{k}' = \mathbf{k} + \mathbf{q}$
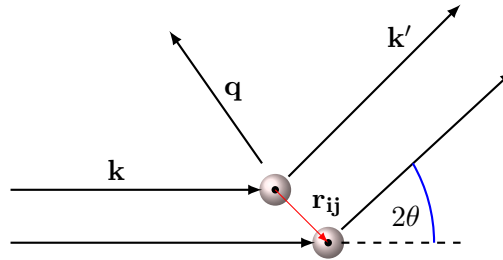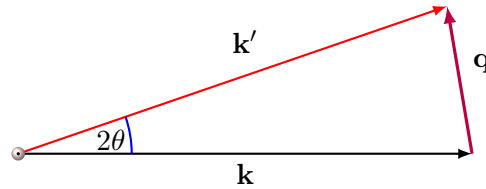
FIGURE 3.2: Wave Vectors

FIGURE 3.3: $\mathbf{k}$ incident, $\mathbf{k}'$ diffracted and $\mathbf{q}$ diffraction vectors

Given that $|\mathbf{k}'| = |\mathbf{k}|$ it is apparent that

$$|\mathbf{q}| = 2|\mathbf{k}| \sin\left(\frac{\mathbf{k}\angle\mathbf{k}'}{2}\right) \tag{3.1.2}$$

Waves incident on the detector, scattered as $\mathbf{q_i}$ and $\mathbf{q_j}$ will interfere and thus a diffraction pattern may form.

3.1.3 Formation of a Diffraction Pattern

We now imagine an ensemble of N identical atoms sitting at 3d positions $\mathbf{r_i}$ from some arbitrary origin $\mathbf{r_0}$ with a detector at a distance much greater than the size of the sample. We may thus approximate the distance from all points to the detector as a constant and ignore the amplitude-distance terms. The position of each detector pixel may be described by $\mathbf{k}'$ with respect to the origin of the sample. At some point $\mathbf{k}'$ on the detector waves scattered from the atoms arrive and interfere. The amplitude of each scattered wave is given by

$$A(\mathbf{k}') = f e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \tag{3.1.3}$$
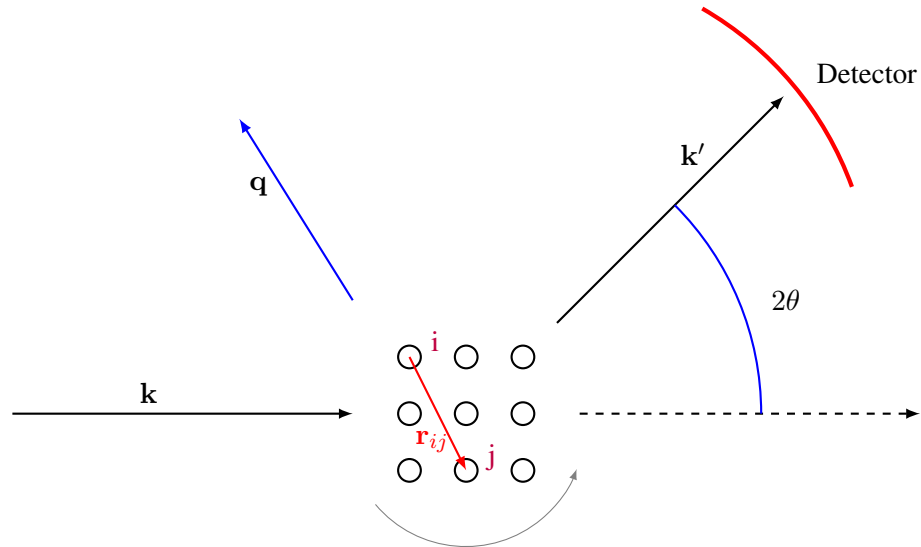
FIGURE 3.4: Diffraction pattern from many sources

As $\mathbf{q} = (\mathbf{k} - \mathbf{k}')$

$$A(\mathbf{q}) = f e^{-i(\mathbf{q} \cdot \mathbf{r})} \qquad (3.1.4)$$

For N scatterers we sum the waves from each scatterer j

$$A(\mathbf{q}) = \sum_{j=1}^{N} f_j e^{-i(\mathbf{q} \cdot \mathbf{r_j})} \qquad (3.1.5)$$

The detector will measure the intensity of the radiation at each pixel summed over all scatterers. This is equal to the square of the scattering amplitude A, being a complex number - strictly the product of the amplitude with its first complex conjugate.

$$I(\mathbf{q}) = |A||A^*| = \sum_{j=1}^{N} \sum_{k=1}^{N} b_j e^{-i \, \mathbf{q} \cdot \mathbf{r_{jk}}} \qquad (3.1.6)$$

The Bragg peaks at $n\lambda = 2d \sin \theta$ give information from long-range ordering. These simulations are concerned with short-range order resulting from growth of crystal domains. The size of domains may be inferred from their broadening of the Bragg peaks using the Scherrer equation

$$\tau = \frac{K\lambda}{\beta \sin \theta} \qquad (3.1.7)$$

where τ is the domain size, K a dimensionless shape parameter generally taken as 0.9. β is the full width - half maximum peak broadening expressed in radians and θ the Bragg angle. ****
image of peak broadening *******

3.1.4 Pair Distribution Functions

The diffraction pattern is a function of the degree of spacial ordering within the sample therefore of the density distribution of scatterers. Taking into account such pair distribution is of particular importance when considering partly ordered systems.

The reduced P.D.F. $g(r)$ is simply the probability of finding a pair of particles at a specific distance r from one another. $g(r)$ is often expressed as the normalised form such that as $r \to \infty, g(r) \to 1$ and for $r <$ distance of closest approach $g(r) = 0$. The pair distribution function may be obtained directly from a M.D. simulation where it is related to the pair density function $\rho(r)$ by $\rho(r) = \rho_0 g(r)$. As $r \to \infty$, $\rho(r)$ will tend to ρ_0, the mean number density of the sample and tend to zero as $r \to 0$

$$g(r) = 4\pi r \left(\rho(r) - \rho_0\right) = 4\pi \rho_0 r \left(g(r) - 1\right) \tag{3.1.8}$$

Within a shell at a range $r_1 \to r_2$ we may specify the number of neighbours, a site's coordination number as

$$N_c = \int_{r_1}^{r_2} R(r)\, dr \tag{3.1.9}$$

In the Debye scattering method the calculation is optimised by 'binning' these coordination numbers in advance then calculating

$$I(q) = \frac{1}{N} \sum_{i=1}^{N} f_i N_{c_i} \frac{sin(2\pi q r_i)}{2\pi q r_i} \tag{3.1.10}$$
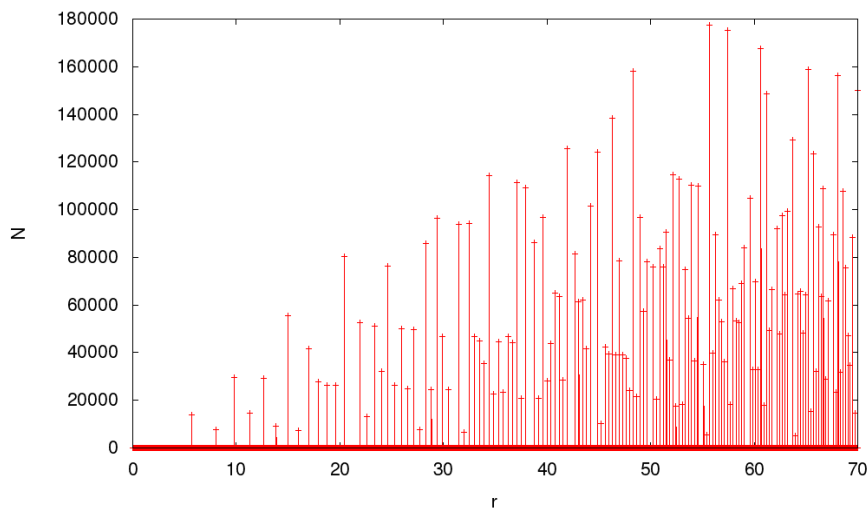

FIGURE 3.5: Example of binned interatomic distances for C=0.29 ordered lattice

We may now specify a radial distribution function $R(r)$ describing the number of atoms in a shell of thickness $d(r)$ at a distance r:-

$$R(r) = 4\pi r^2 \rho(r) \qquad (3.1.11)$$

giving

$$g(r) = \frac{R(r)}{r} - 4\pi r \rho_0 \qquad (3.1.12)$$

This may be easily determined at any point in a molecular dynamics simulation. If we assume initially that atoms sit at precise positions $\mathbf{r_i}$ without thermal or other displacements then their positions may be expressed as a series of delta functions $\delta(\mathbf{r_0} - \mathbf{r_i})$. Setting $\mathbf{r_0} = 0$ gives

$$R(r) = \frac{1}{N} \sum_i \sum_j \delta(\mathbf{r_{ij}}) \qquad (3.1.13)$$

The reduced pair distribution function $g(r)$ is the Fourier Transform of $S(q)$ the total scattering structure function – effectively the normalised diffraction pattern.

$$G(r) = \frac{2}{\pi} \int_{qmin}^{qmax} q[S(\mathbf{q}) - 1]sin(qr)dq \qquad (3.1.14)$$

The inverse transform is more useful here

$$S(q) = 1 + \frac{1}{q} \int_0^\infty r(r)sin(qr)dr \qquad (3.1.15)$$

3.1.5 The Role of Reciprocal Space

Reciprocal space (also *momentum space, k-space* is a convenient abstraction when considering diffraction from a periodic structure being the Fourier transform of the real space *direct* lattice. Points in reciprocal space represent families of planes in the direct lattice. A key feature being that the vector direction between any two point in the reciprocal lattice represents the direction between two planes in the direct lattice. The magnitude of the reciprocal vector is the reciprocal of the interplanar spacing. Expressing these reciprocal lattice vector lengths as $|\mathbf{G}| = \frac{2\pi}{\lambda}$ gives the distance in radians per unit length.

If we have a set of atomic positions in real space $\mathbf{r_i} = (h\mathbf{x_i} + k\mathbf{y_i} + l\mathbf{z_i})$ then the Fourier transform is given by

$$f(\mathbf{r}) = \sum_G f(\mathbf{G})e^{i(\mathbf{G} \cdot \mathbf{r})} \qquad (3.1.16)$$

The key point here is that this transform maps directly the diffraction pattern from the scatterers i.e.

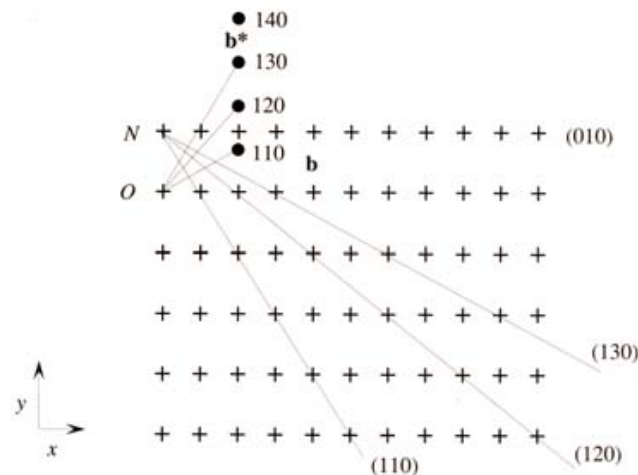$$S(\mathbf{q}) = \sum_{i,j,k} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{3.1.17}$$

FIGURE 3.6: Construction of the Reciprocal Lattice.

Real space points are +, reciprocal points ·

The reciprocal lattice axis vectors are given by

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \tag{3.1.18}$$

Note that $\mathbf{b}_1$ is orthogonal to both $\mathbf{a}_2$ and $\mathbf{a}_3$, $\mathbf{b}_2$ is to both $\mathbf{a}_1$ and $\mathbf{a}_3$ and so on. Points in the reciprocal lattice are mapped as

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \tag{3.1.19}$$

As is generally accepted diffraction peaks occur when $\mathbf{q} = \mathbf{G}$. [70]

3.2 Simulating a Diffraction Pattern

Given a known crystal structure one may calculate the reflections from specific planes - the inverse of conventional experimental crystallography. The alternate approach, used here is to calculate the diffraction pattern from a set of atomic positions mirroring the physical processes in experimental x-ray or neutron crystallography. Such an *a priori* technique makes few of the

assumptions of conventional crystallography such as 'reflection from planes' though is computationally somewhat expensive. Since we are considering an *a priori* algorithm it may be helpful to initially limit standard crystallographic terminology and formulate the problem in general physical terms.

We wish to simulate the diffraction pattern formed when a beam of radiation is incident upon group of atoms. These scatterers interact with the incident radiation resonating and emitting spherical wavefronts. Different scatterers will have different scattering powers. Here we are only considering scattering by Hydrogen so this scattering *factor* can be set to unity. A number of methods have been developed to simulate diffraction patterns directly from atomistic data.

The most direct takes a rather *brute force* approach. One simply determines the linear path lengths from a monochromatic coherent radiation source to each atom in the model and from there to every pixel on the detector array . Sin 2π and cos 2π of $n\lambda$ for each path are summed at each pixel giving the resultant amplitude and phase. This scales directly with $N_{atoms} \times n_{pixels}$, for a sample of 10^6 atoms and a linear detector of 10^4 pixels one has of the order of 10^{10} iterations - perfectly acceptable on a modern workstation. Since each calculation does not depend on the others then this is easily optimised by parallel processing. One problem here though is the need for the paths lengths to be very long compared to the size of the sample and hence the differences in atomic positions. This to avoid distortion of the pattern by some parts of the sample being significantly closer to the detector than others. If the simulation mirrors a real diffractometer the sample $\rightarrow$ detector distance will be $> 10^8\times$ the inter-atomic spacing. Assuming that we need to resolve path differences of 10^{-2} of this spacing we require a precision of $1 : 10^{10}$. To overcome this one needs to use high precision 'long' real numbers which significantly slows computation.

A more sophisticated approach involves calculating

$$I(\mathbf{k}') = \sum_{i \neq j} \sum_{j} e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \tag{3.2.1}$$

to every point on the detector array (fig: 3.4). If we assume that to the incoming radiation each atom acts as a point scatterer and that the atoms do not move their positions may be represented as a series of δ-functions. A further simplification may be introduced in assuming that the size of the region being sampled is much smaller than the distance between the sample and the detector. Thus we can assume that the scattering distance and angle from each atom to each point on the detector are approximately constant. The problem with this method again computational load. For a sample of 10^5 atoms and a 2d detector of 10^6 pixels one would need to perform some 10^{16} calculations before needing to rotate the sample to ensure that all possible peaks are detected. Without optimisation this is impractical. This has the appearance of Fourier transform and so it should be practical to perform an F.F.T. if we assume that the scatterers are both point entities

and sit on points fixed on a regular 3d lattice. If the points are permitted to displace from these regular point, via thermal vibration or during diffusion one cannot perform an FFT. This could be addressed by defining a grid whose spacing is much smaller than the lattice parameter and limiting scatters to these discrete positions. With say 10^6 atoms and 10 intermediate points between the *regular* lattice sites results a grid of 10^9 points with only 0.1% filled at any time. This will lead to very large data arrays which without some optimisation will again add to computation time.

In the 1980s a simulation technique using the Debye scattering equation for powder samples was developed.

$$I(q) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j \frac{sin(2\pi q r_{ij})}{2\pi q r_{ij}} \qquad (3.2.2)$$

where f_i, f_j are the scattering factors of the respective atoms and q, r_{ij} are equal to $|\mathbf{q}|$ and $|\mathbf{r_{ij}}|$ respectively. The algorithm may be optimised by binning the distances r_{ij} before performing
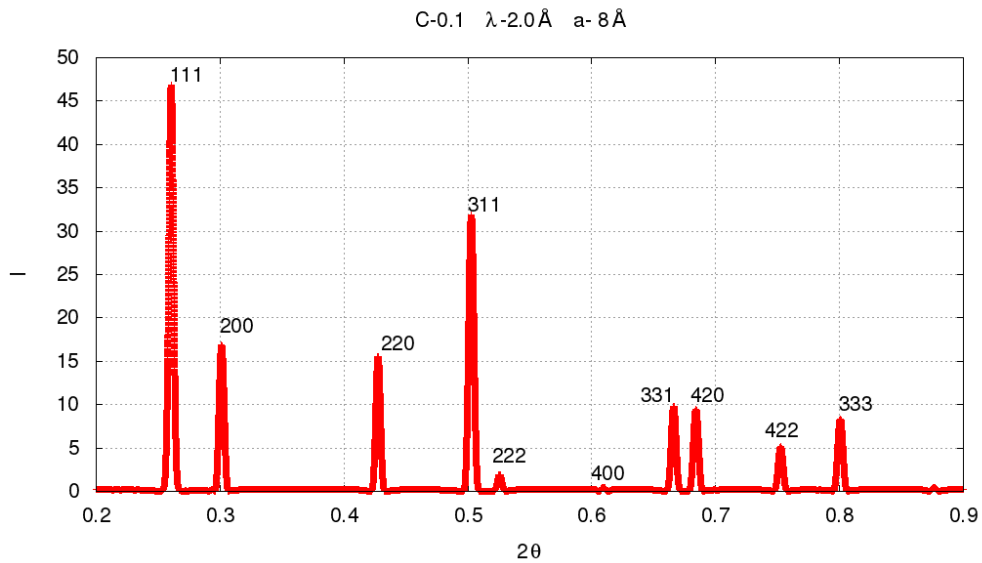

FIGURE 3.7: Virtual Debye Diffraction Pattern demonstrating only (hkl) all odd or all even as expected for FCC structure

the computational intensive sin calculations. With sufficiently narrow bins errors generated are minimal (fig (3.5). In effect this technique loses the absolute spacial, i.e. directional, information in favour of computationally faster method of generating pair distributions (the bins). The size of crystal regions may be inferred from peak broadening rather than being directly observed. This technique is very fast, on a 3 GHz workstation a pattern from 10^4 atoms, with 10^4 detector pixels and 10^5 bins computes in some 100 seconds(fig 3.7). Scaling to a more realistic 10^6 atoms takes $\sim$ 3 hours.

The technique used here for the contour 2d plots involves summing $e^{i(\mathbf{G}\cdot\mathbf{r}_i)}$ over a range of G_x and G_y (fig 3.8).
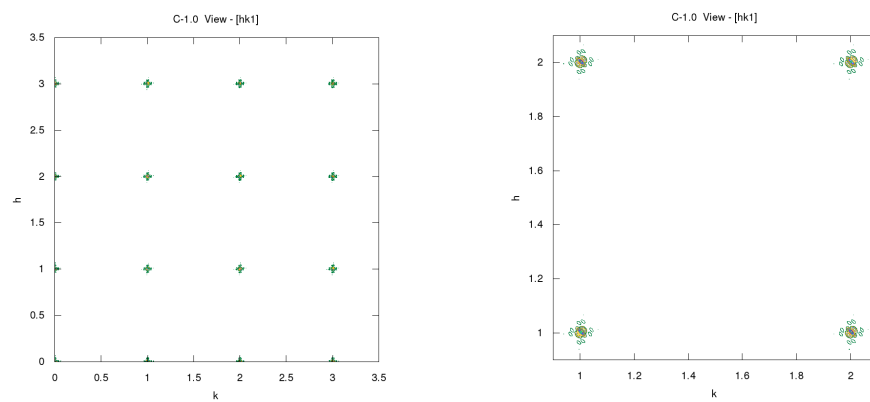
FIGURE 3.8: 2d contour plots of partly filled lattice in (hk1)

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