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Exercise sheet 4

https://wiki.mlz-garching.de/n-lecture06:index

Solutions

1. 1D Reciprocal Lattice

For the scattering computations from a simple cubic lattice, so far, we have simplified the crystal to a 1 dimensional lattice, with point-like atoms at equal distance. Instead of computing the scattering pattern by summing up over all scattered waves, we have learned in the lecture, that the scattering function is also given by the Fourier transform of the scattering structure in real space.

Assume a 1D chain of point-like atoms (delta functions) with distance d and follow the steps below.

- Express the linear chain of Atoms in form of a function f(r).
- Form the Fourier transform of this function and evaluate it by assuming an infinite number of atoms. What is the meaning of k?

$$FT(f(r)) = f(k) = \frac{1}{\sqrt{2\pi}} \int f(r)exp(-ikr)dr$$

- The Fourier transform will have the same general form as the real space function with a different spacing p. How are d and p related?
- (optional) Compute the Fourier transform for limited numbers of Atoms in the chain and compare it to the results previously obtained by Bragg scattering.

Solution

• The linear chain of atoms can be represented by an infinite sum over delta functions at integer multiples of the distance d:

$$f(r) = \sum_{n=-\inf}^{\inf} \delta(r - R_n)$$
, with $R_n = n \cdot d$

• For calculating the Fourier transform we first use, that we can commute the sum and integration, and easily evaluate the integral:

$$FT(f(r)) = f(k) = \frac{1}{\sqrt{2\pi}} \int f(r)exp(-ikr)dr$$
$$= \frac{1}{\sqrt{2\pi}} \int \sum_{n=-\inf}^{\inf} \delta(r-nd)exp(-ikr)dr$$
$$= \frac{1}{\sqrt{2\pi}} \sum_{n=-\inf}^{\inf} \int \delta(r-nd)exp(-ikr)dr$$

$$=\frac{1}{\sqrt{2\pi}}\sum_{n=-\inf}^{\inf}exp(-inkd)$$

For the next step, the infinite sum has to be evaluated. Mathematically, we can look at the limit of the sum:

$$\lim_{N \to \infty} \sum_{n=-N}^{N} exp(-inkd) = \lim_{N \to \infty} \sum_{n=0}^{N} exp(-inkd) + \sum_{n=1}^{N} exp(+inkd)$$
$$= \lim_{N \to \infty} \sum_{n=0}^{N} exp(-inkd) + \sum_{n=0}^{N} exp(+inkd) - 1 = 1 + 2sum_{n=1}^{N} cos(kd)$$
$$= \lim_{N \to \infty} \frac{sin((N+1/2)kd)}{sin(kd/2)}$$

in the last step we used the Dirichlet Kernel, which in the limit of $N \rightarrow$ inf becomes effectively a sum of delta functions at the positions $kd = 2m\pi$ with *m* integer. This is exactly the definition of the reciprocal lattice positions (or reciprocal vectors in higher dimensions). There is a normalization term involved in the limit, which we ignore at this moment. With this result, we get

$$\approx \sum_{m=-\inf}^{\inf} \delta(k - K_m)$$
, with $K_m = m \frac{2\pi}{d} = m \cdot p$

which has the same shape as the real space function, just with a different spacing p.

For a better understanding of the infinite sum of complex exponentials think about the following two cases:

- 1. for any case with $k = 2\pi/d$, the exponential function exp(-inkd) = 1 for all n. At these k-values the Fourier transform adds up to infinity, which in the limit we identify with a delta function
- 2. for any other case, $k \neq 2\pi/d$, the exponential function gives a unitvector in the complex plane. When performing the infinite sum over n, the resulting vectors for a single k will cancel each other and the fourier transform is equal to zero. (In some cases the vectors will only have a limited set of directions, e.g. for $k = \pi/d$, while other k-values result in arbitrary directions with a statistical mean value of zero)
- The computations for a limited set of atoms is, of course, identical to the geometric if we look at the scattering intensity $I = |f(r)|^2$. However we get additional insight in the functan as we can have a look at the real and imaginary part. Shown below is an example for N = 10.



2. Ambiguity of the Scattering Intensity

In a scattering experiment, we can only measure the scattering intensity $I(k) = |f(k)|^2$. Since f(k) is complex, we lose a part of the information contained in it, i.e. the imaginary part (or phase). To illustrate this, we take a look at a small chain of 4 atoms which have a gaussian shape:

$$f_l(x) = \frac{1}{\sqrt{2\pi\sigma_l^2}} exp\left(\frac{-(x-r_l)^2}{2\sigma_l^2}\right)$$

where each atom l has a position r_l and a standard deviation σ_l . The scattering pattern is again given by the Fourier transform FT(f(x)) = f(k), with the Fourier transform of a single gaussian:

$$FT(f_l(x)) = f_l(k) = \exp\left(-ikr_l\right)\exp\left(\left(\frac{-1}{2}\sigma_l k\right)^2\right)$$

Compute the scattering function f(k) and visualize the Intensity, real part and imaginary part and compare them for the following cases:

- All 4 atoms are equidistant with $d = 3\text{\AA}$ and have the same shape $\sigma_l = 0.5$.
- As before, but shift all atoms by 1Å.
- All atoms are equidistant, but have a different shape $\sigma_l = [0.1, 0.2, 0.3, 0.4]$ Å.
- As before, but reverse the order of σ_l

Solution

Both the real-space and k-space functions are given by the sum of the contributions from each individual atom.

$$f(x) = \sum f_l(x) , f(k) = FT(f(x)) = \sum f_l(k)$$

- For Case 1 and 2, with identical atoms and lattice distance but a shift of the atoms the Observed scattering intensity $(I = |f(k)|^2)$ is identical as well as the complex function f(k).
- Cases 3 and 4 consist of different atoms with reversed order. Again, the scattering intensity is identical for both cases, but now the real and imaginary part of f(k) are quite different.
- (additional) Case 5 compares two permutations of case 3 (or 4). Here, the large peaks of $|f(x)|^2$ are identical, however, the spaces inbetween show a different behaviour. In contrast, the real and imaginary part of f(k) are vastly different from each other.
- (additional) Case 6 shows a comparison between identical atoms, with $\sigma = 0.2$ Åand $\sigma = 0.4$ Å. In this case, all peak positions of $|f(k)|^2$ are identical but the intensity is different. The 'size' of the atoms can be determined by the envelope function of peak intensities. The same behaviour is observed for the complex f(k)







3. 2D Reciprocal Lattice

Now, we go a step further and consider a two dimensional rectangular lattice of point-like atoms (delta functions) with lattice distances $d_x = 2\text{\AA}$ in x-direction and $d_y = 3\text{\AA}$ in y-direction. The positions of all atoms are now $r_l = m_l \vec{a}_1 + n_l \vec{a}_2$ with integers m_l , n_l and the basis vectors of the lattice \vec{a}_1 and \vec{a}_2 :

$$\vec{a}_1 = \left(\begin{array}{c} d_x \\ 0 \end{array} \right) \ , \ \vec{a}_2 = \left(\begin{array}{c} 0 \\ d_y \end{array} \right)$$

Analogous to the 1D case, this 2D lattice can be formulated as a function $f(\vec{r})$ and Fourier transformed to obtain the scattering function $f(\vec{k})$. The result is again a regular structure which is called the reciprocal lattice of the crystal. The basis vectors of the reciprocal lattice \vec{b}_1 and \vec{b}_2 are then defined such that:

$$\vec{a}_l \cdot \vec{b}_m = 2\pi \delta_{lm}$$

- Draw the real and reciprocal lattice.
- What does the crystal unit cell and first Brillouin zone look like?
- In the real lattice, each point represents the position of an atom. What is the meaning of each point in the reciprocal lattice?
- Repeat the previous steps for a hexagonal lattice with lattice distance d = 3Å.

Solution

• With the given formula, the basis vectors of the reciprocal lattice are:

$$\vec{b}_1 = \begin{pmatrix} p_x \\ 0 \end{pmatrix}$$
, $\vec{b}_2 = \begin{pmatrix} 0 \\ p_y \end{pmatrix}$, with
 $p_x = \frac{2\pi}{d_x} = 2.09/\text{\AA}$, $p_y = \frac{2\pi}{d_y} = 3.14/\text{\AA}$

as the reciprocal lattice distances. Additionally, we can take a look at the Area , the basis of both lattices are spanning:



- The points in a reciprocal lattice give the possible Bragg peaks in terms of vavevector transfer (momentum transfer) between the incoming and scattered neutron. The positions of the reciprocal lattice are independent from the neutron wavelength, however, the Bragg peaks observed in an experiment and the respective scattering angle will depend on the chosen wavelength.
- The basis vectors for a hexagonal lattice are given by:

$$\vec{a}_1 = d \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
, $\vec{a}_2 = \frac{d}{2} \begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix}$

and the reciprocal lattice vectors can be calculated again by using $\vec{a}_l \cdot \vec{b}_m = 2\pi \delta_{lm}$:

$$\vec{b}_1 = \frac{2\pi}{\sqrt{3}d} \begin{pmatrix} \sqrt{3} \\ 1 \end{pmatrix}$$
, $\vec{b}_2 = \frac{4\pi}{\sqrt{3}d} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

For the areas in real and reciprocal space we find the same relation as for the rectangular case:



4. Internal Structure

The previous example of a 2D crystal lattice assumed point like atoms, which is reasonable if we only consider the size of a nucleus (and its interaction potential) compared to the neutron wavelength. However, in real materials this assumption is typically not correct. Possible reasons might be a crystal with more than one Atom per unit cell or scatterers which are not atoms at all, e.g. larger molecules or magnetic structures. Similarly, thermal motion of the atoms can be described by an effective gaussian shape which is normally accounted for by the Debye-Waller factor.

Consider the rectangular 2D lattice from the previous exercise, but now with three Atoms per unit cell. Atom 1 is positioned directly at the lattice points $\vec{u}_1 = 0$, while atoms 2 and 3 are at the relative positions $\vec{u}_2 = 0.4\vec{a}_1$ and $\vec{u}_3 = 0.6\vec{a}_2$.

- The real space lattice is now given by the convolution of two functions $f(\vec{r}) = S(\vec{r}) \otimes F(\vec{r})$. $S(\vec{r})$ describes the periodic structure of the lattice and is identical to lattice described in exercise 3. $F(\vec{r})$ describes the arrangement of atoms in a single unit cell (the positions of the atoms 1, 2 and 3). Draw the real space lattice and formulate the functions $S(\vec{r})$ and $F(\vec{r})$
- How are the Fourier transforms $S(\vec{k})$ and $F(\vec{k})$ related in the scattering function $f(\vec{k})$?
- How is the intensity measured in an experiment (qualitatively) changed in comparison to exercise 3?

Solution

$$S(\vec{r}) = \sum_{l,m=-\inf}^{\inf} \delta(\vec{r} - l \cdot \vec{a}_1 - m \cdot \vec{a}_2)$$
$$F(\vec{r}) = \delta(\vec{r} - \vec{u}_1) + \delta(\vec{r} - \vec{u}_2) + \delta(\vec{r}\vec{u}_3)$$

The convolution theorem states, that

$$FT(f(x) \otimes g(x)) = FT(f(x)) \cdot FT(g(x))$$

which means in our case, that

$$f(\vec{k}) = FT(f(\vec{r})) = FT(S(\vec{r}) \otimes F(\vec{r})) = FT(S(\vec{r})) \cdot FT(F(\vec{r})) = S(\vec{k}) \cdot F(\vec{k})$$

Generally speaking, $S(\vec{r})$ tells us about the arrangement of atoms, particles, unitcells in a crystal, ect. while $F(\vec{r})$ describes how a single of those units looks like. If we look at the present case of a crystal with multiatom unitcell, the convolution of both functions creates new deltapeaks in the lattice. In Reciprocal space, $S(\vec{k})$ is again in the form of a lattice, while $F(\vec{k})$ is typically a rather broad and continuous function. This means, that $F(\vec{k})$ only affects the intensity of Bragg peaks defined by $S(\vec{k})$, instead of adding new positions. In Experiment this means, that the periodic structure of a crystal is in most cases easily measured, while it is very difficult to identify the inner structure of a unit Cell.



