

Lecture 1: Reciprocal space

Our goal in this course is to review the methods by which chemists have managed, over the past century, to determine the atomic-level structure of materials. Much of this builds on the basic introduction to crystallography and diffraction given in the IA course, but we are going to deal with the concepts involved on a slightly deeper level. We will begin by revisiting the diffraction process itself, recasting our understanding in terms of “reciprocal space” — a topic that forms the subject of this first lecture.

In order to understand how diffraction really works, we need some idea of how waves interact with matter. And the key is to think of the arrangement of atoms in a material as a set of waves itself. A bizarre concept, perhaps. But actually atoms are small enough that the “particle-like” descriptions of structure we might instinctively seek to use — density at a given position in space — are no more real than the “wave-like” concepts of amplitude and periodicity. It would seem strange, for example, to describe a wave on a body of water in terms of a “mass”, or to locate it at a precise point in space. The same is true of the radiation one uses in a diffraction experiment, and in some senses the same is true even of individual atoms. While our intuition lives in “real space”, where structure is a density function $\rho(\mathbf{r})$ that characterises how much matter is at a given point \mathbf{r} , what we will develop in this lecture is a feel for “reciprocal space”, where structure is defined instead in terms of a function $F(\mathbf{Q})$ that tells us what components of waves of periodicity \mathbf{Q} are required to produce the same arrangement of atoms.

Let us first formalise what we mean by periodicity. Here there are two concepts: a wave repeats after a given distance, called the wavelength λ , and a wave propagates along a particular direction. So by saying a wave has the periodicity \mathbf{Q} we are defining $Q = |\mathbf{Q}| = 2\pi/\lambda$ and assigning the direction \mathbf{Q}/Q to be the same as the direction of propagation of the wave. Mathematically, we would represent the wave by the function $\psi(\mathbf{r}) = \exp(i\mathbf{Q} \cdot \mathbf{r})$. Note that this function repeats every time that $\mathbf{Q} \cdot \mathbf{r}$ increases by another multiple of 2π , which will occur for each wavelength λ added to \mathbf{r} in a direction parallel to \mathbf{Q} . This is what we mean by a wave of wavelength λ that propagates parallel to \mathbf{Q} .

A key point is that large values of Q correspond to waves with very small wavelengths, while small values of Q correspond to waves with long wavelengths. So, perhaps counterintuitively, as we add waves of larger and larger values of Q to assemble our material structure, we are actually making finer- and finer-scale adjustments in real space. The broadest features in real-space will be described by waves of smallest Q values in reciprocal space. Note also that the units of Q are inverse length (usually \AA^{-1} , since we will be using \AA as units for structure on the atomic scale). So when we speak of reciprocal space, we are using inverse lengths as our units.

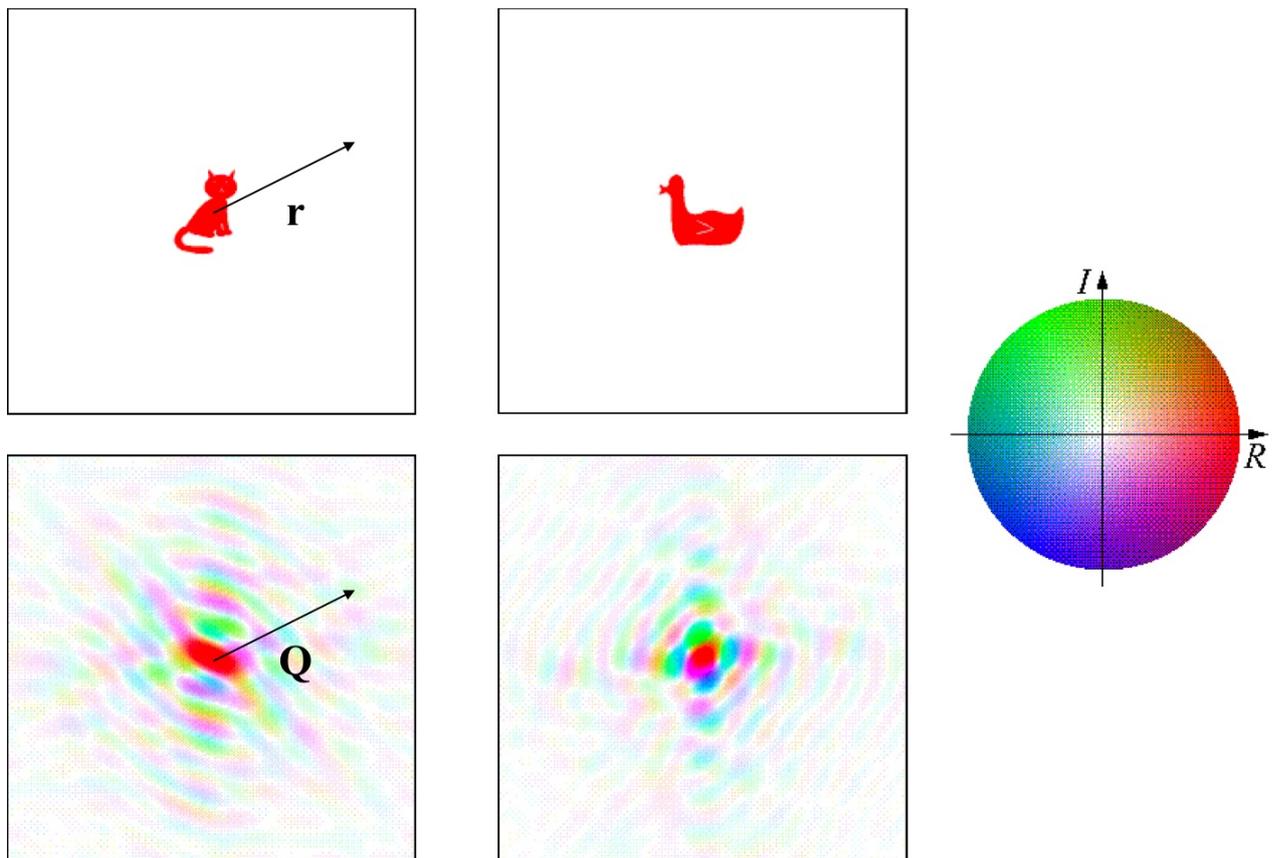
The conversion itself between real space and reciprocal space is relatively straightforward. As we said above, our reciprocal space function $F(\mathbf{Q})$ is meant to tell us what components of waves of periodicity \mathbf{Q} are needed to produce the real-space density function $\rho(\mathbf{r})$. This is precisely the mapping described by Fourier transforms, which tell us how to deconstruct any function into an equivalent set of waves of different periodicities. The mathematics gives us then:

$$F(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) \, d\mathbf{r}, \quad (1)$$

$$\rho(\mathbf{r}) = \frac{1}{2\pi} \int F(\mathbf{Q}) \exp(-i\mathbf{Q} \cdot \mathbf{r}) \, d\mathbf{Q}. \quad (2)$$

We will see in the next lecture that what diffraction does is to give us a way of measuring $F(\mathbf{Q})$ (or, at least, related functions). In principle, if we measure $F(\mathbf{Q})$ for sufficiently many values of \mathbf{Q} then we could use the reverse Fourier transform (equation (2) above) to reconstruct the distribution function $\rho(\mathbf{r})$. This is the underlying idea of crystallography. There are problems along the way, and we will deal with these as we come to them. But for the time being what is most important is for us to develop an intuition for what $F(\mathbf{Q})$ looks like for different systems — how it is related to $\rho(\mathbf{r})$ and what it can tell us in itself about material structure.

Perhaps the first thing to note about $F(\mathbf{Q})$ is that it is a complex number (even given that the real-space distribution $\rho(\mathbf{r})$ is real, and positive, everywhere). As such, we can think separately about its magnitude $|F(\mathbf{Q})|$ and its complex argument ϕ , which we call its “phase”; that is, $F(\mathbf{Q}) = |F(\mathbf{Q})| \times \exp(i\phi)$. We will use a very convenient method of representing both of these components pictorially (see following figure), where a diagram of reciprocal space is coloured such that the intensity at a given point \mathbf{Q} corresponds to the magnitude of $F(\mathbf{Q})$, and the colour tells us about the phase ϕ .



What we have done in this picture is to take the Fourier transform of an image of a cat and of an image of a duck. The real-space distribution functions have been simplified in each case such that $\rho(\mathbf{r})$ is either 1 (if some part of a duck or a cat indeed exists at the point \mathbf{r}) or 0 (if the point \mathbf{r} is animal-less). Of course both \mathbf{r} and \mathbf{Q} are two-dimensional vectors in this case, but everything we notice will apply equally well to three dimensions. Let us make some observations:

- (i) The Fourier transforms look neither like a cat nor like a duck.
- (ii) In both cases, there is a “blob” near $\mathbf{Q} = 0$ that has the same phase ($\phi \sim 0$).
- (iii) There is a kind of symmetry — despite the obvious lack of symmetry in real-space — in that the arm-like feature to the top-left of the cat Fourier transform is mirrored by a similar feature to the bottom-right, with the phases reversed between the two. The same type of relation can be seen throughout both patterns.
- (iv) The magnitudes of $F(\mathbf{Q})$ tend to decrease with increasing Q .

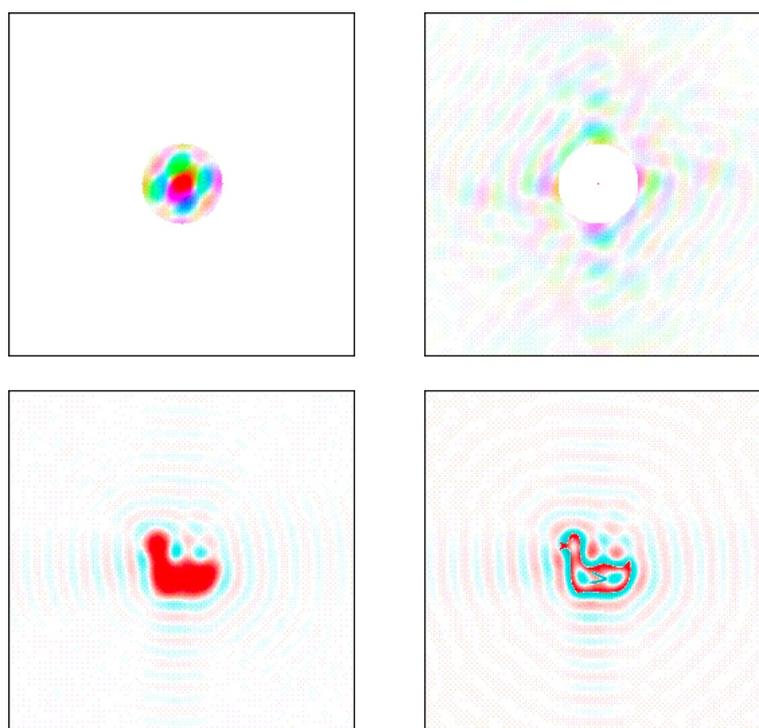
Our first observation is reassuring, because it tells us that we do indeed need to think about Fourier transforms: they will rarely be obvious to us. Point (ii) also makes sense if we consider how equation (1) simplifies as $\mathbf{Q} \rightarrow 0$: in this limit we obtain $F(0) = \int \rho(\mathbf{r}) \, d\mathbf{r}$, which is of course just the total density in the entire real space function — namely, the amount

of cat or the amount of duck. Since both are positive and real, we expect a positive and real value for $F(0)$; hence the graphical Fourier transforms are intense and red-coloured at their centres. Our statement with regard to symmetry also follows from equation (1) if we consider the relationship between $F(\mathbf{Q})$ and $F(-\mathbf{Q})$:

$$F(-\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{Q}) \, d\mathbf{r} = \left[\int \rho(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) \, d\mathbf{r} \right]^* = [F(\mathbf{Q})]^*, \quad (3)$$

where the asterisk notation represents the operation of complex conjugation. Hence the magnitudes of $F(\mathbf{Q})$ and $F(-\mathbf{Q})$ are identical, and their phases reversed. This rule is known as “Friedel’s law”, which also demands that $F(0)$ must be real.

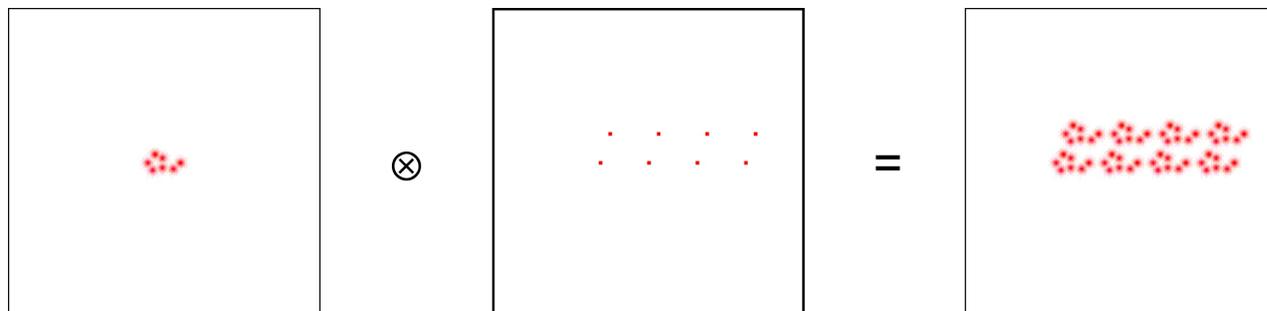
To understand the last of our four observations, we must recall our statements above concerning the meaning of $F(\mathbf{Q})$ at large Q . The bulk of the density in real space — the fact that, for either cat or duck, we basically have a collection of density near the origin and not much else — will be recovered from the long-wavelength information near $\mathbf{Q} = 0$. The high-frequency information at larger Q will help separate the cat’s tail from its body, or will give the duck its beak and wings. This sort of detail concerns less and less density in real space, and so the components of the waves required will decrease with increasing Q .



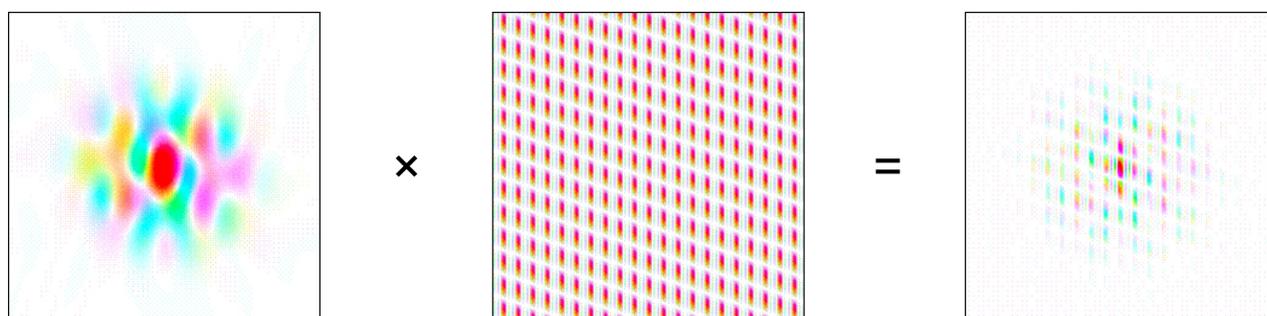
In the picture above we have illustrated this by calculating the reverse Fourier transform of the duck image with different parts of reciprocal space excluded. If we use just the low Q region (left hand side in the image above), then we get the broad features of the duck; if we use just the high Q region, then we obtain the edges. Indeed these approaches are used in image processing for compression (low Q filtering) or to determine edges (high Q).

A useful mathematical concept when dealing with Fourier transforms is called convolution and is a little strange. It is the idea of combining two functions such that we place a copy

of one function at each point in space, weighted by the value of the second function at the same point. The mathematics is dealt with separately in the appendix, but the concept (which is all that is important) is explained more satisfactorily through a diagram.



On the left hand side we have two density functions: the first might reasonably represent a single molecule, while the second is just a set of points. What the convolution of these two functions does is to place a copy of the molecule at each point in the set (or, equivalently, to copy the set of points for each atom in the molecule). We end up with a set of molecules, whose spacing is determined by the original set of points. The convolution operation itself is represented by the operator \otimes , and is quite useful because it enables us to deconstruct a complex object (a group of molecules) into two simpler objects: a single molecule and an array of points. But it is even more useful in the current context, because the Fourier transform of a convolution is equivalent to the product of the individual Fourier transforms. Let us see this pictorially in terms of the Fourier transforms of the above images:



Note that the Fourier transform of the grid of points is itself real-valued everywhere, so that the phases in the final result come directly from the phases for the individual molecule. So on the one hand the phases are telling us something about the molecule, while on the other hand the grid-like pattern is telling us about how the molecules are repeated in real space.

Of course, the essential feature that distinguishes the crystalline form as a state of matter is the existence, on the atomic scale, of some recurring structural unit — be it a single atom or a group of atoms — whose repeat extends at regular intervals in all three dimensions. As we know, the crystal is built up from from a tessellation of these identical unit cells, such that the contents of any one unit cell can be mapped directly onto the contents of another through translations alone.

Here is where the concept of convolution is so useful: it enables us to consider an entire crystal lattice as the contents of a single unit cell (the “motif”) *convoluted with* a lattice of points that describes the tessellation itself — how the unit cells are stacked together to form the crystal. In order to understand the Fourier transform of a crystal, all we need is to understand the Fourier transform of the motif and the Fourier transform of the lattice of points. We can take the product of these two transforms to arrive at the Fourier transform of the crystal itself.

So the question now is to ask what the Fourier transform of a lattice actually looks like. To answer this, let us first define the lattice mathematically as a series of delta-functions located at integral combinations of the unit cell vectors \mathbf{a} , \mathbf{b} and \mathbf{c} :

$$\mathcal{L}(\mathbf{r}) = \sum_{UVW} \delta[\mathbf{r} - (U\mathbf{a} + V\mathbf{b} + W\mathbf{c})]. \quad (4)$$

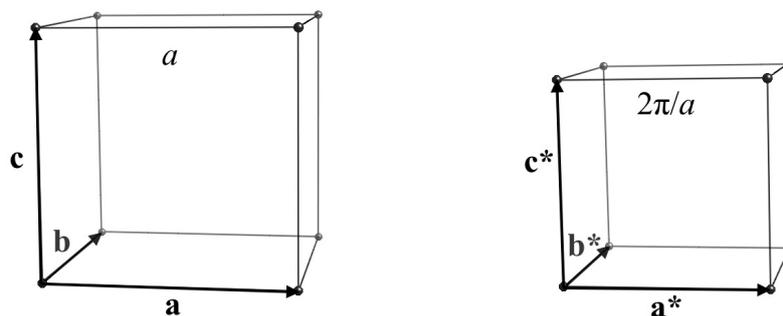
We could do the mathematics (and indeed all is written out in gory detail in the appendix), and calculate the Fourier transform $\mathcal{R}(\mathbf{Q}) = \int \sum_{UVW} \delta[\mathbf{r} - (U\mathbf{a} + V\mathbf{b} + W\mathbf{c})] \exp(i\mathbf{Q} \cdot \mathbf{r}) \, d\mathbf{r}$ directly. The result is a lattice itself, now running throughout reciprocal space:

$$\mathcal{R}(\mathbf{Q}) = \sum_{hkl} \delta[\mathbf{Q} - (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)]. \quad (5)$$

Here the “reciprocal lattice vectors” \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* generate this “reciprocal lattice”:

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})}, \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})}. \quad (6)$$

These equations look more complicated than they actually are. Their derivation is given in the appendix, but we are really only concerned with their meaning (the important thing, after all). In each case, the cross product contained in the numerator produces a vector that is perpendicular to the two real-space axes involved. That is, $\mathbf{b} \times \mathbf{c}$ — and hence \mathbf{a}^* — is perpendicular to \mathbf{b} and \mathbf{c} . In cases where \mathbf{a} , \mathbf{b} and \mathbf{c} are not orthogonal (such as in hexagonal systems), then \mathbf{a}^* may not necessarily be parallel to \mathbf{a} , and so on. The denominator is actually the same value in each case: namely, the unit cell volume. It scales the vector to the correct length, and it’s not too hard to see that in simple systems we end up with intuitive results.



Let us consider the case of a simple cubic lattice, illustrated above. The solid points in this picture correspond to three-dimensional delta functions $\delta(\mathbf{r})$, and the unit cell vectors are aligned with cartesian axes $\mathbf{i}, \mathbf{j}, \mathbf{k}$ such that $\mathbf{a} = a\mathbf{i}$, $\mathbf{b} = a\mathbf{j}$ and $\mathbf{c} = a\mathbf{k}$. In evaluating the reciprocal lattice, we find (e.g.) $\mathbf{b} \times \mathbf{c} = a^2\mathbf{i}$, and that $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = a^3$. Substituting these values into the equation for \mathbf{a}^* given in (6), one obtains $\mathbf{a}^* = \frac{2\pi}{a}\mathbf{i}$. Similarly, $\mathbf{b}^* = \frac{2\pi}{a}\mathbf{j}$ and $\mathbf{c}^* = \frac{2\pi}{a}\mathbf{k}$. So, the reciprocal lattice is also a cubic lattice, but now with a edge length of $2\pi/a$. The larger the real space unit cell, the smaller the reciprocal space unit cell.

A summary of some simple lattice \leftrightarrow reciprocal lattice relationships is as follows:

- P cubic lattice of side $a \leftrightarrow$ P cubic reciprocal lattice of side $a^* = 2\pi/a$
- F cubic lattice of side $a \leftrightarrow$ I cubic reciprocal lattice of side $2a^* = \pi/a$
- I cubic lattice of side $a \leftrightarrow$ F cubic reciprocal lattice of side $2a^* = \pi/a$
- Tetragonal lattice with $c > a \leftrightarrow$ tetragonal reciprocal lattice with $c^* < a^*$
- Hexagonal lattice with $c > a \leftrightarrow$ hexagonal reciprocal lattice with $c^* < a^*$

We can already say something about the Fourier transform we expect for a crystal. *Irrespective* of the chemical composition, or the arrangement of atoms within the unit cell, we know that the Fourier transform will be the product of the transform of the motif and the that of the lattice. We now know that the latter is itself a lattice — zero nearly everywhere in reciprocal space, except at each of the reciprocal lattice points. So the total product must also be zero nearly everywhere: it too will look like a lattice, except that the values at each of the lattice points will be determined by the Fourier transform of the motif at the same points in reciprocal space. Writing this in terms of equation (1), we have:

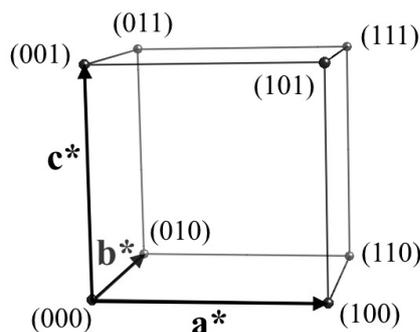
$$F_{\text{crystal}}(\mathbf{Q}) = F_{\text{unitcell}}(\mathbf{Q}) \times \mathcal{R}(\mathbf{Q}) \quad (7)$$

$$= \int_{\text{unitcell}} \rho(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) \, d\mathbf{r} \times \sum_{hkl} \delta[\mathbf{Q} - (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)], \quad (8)$$

which is only non-zero for $\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$. Expanding each point \mathbf{r} in terms of its components x, y, z along the real-space unit cell vectors, we have:

$$F_{\text{crystal}}(hkl) = \int_{\text{unitcell}} \rho(\mathbf{r}) \exp[i(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})] d\mathbf{r} \quad (9)$$

$$= \int_{\text{unitcell}} \rho(\mathbf{r}) \exp[2\pi i(hx + ky + lz)] d\mathbf{r}. \quad (10)$$



We finish this lecture by commenting that it is customary to label reciprocal lattice points by the corresponding values h, k, l , using the notation (hkl) as in the figure above. This is the notation used in powder diffraction (*e.g.* as you will meet — or already will have met — in the IA course) and we will discuss it further in the next lecture. Indeed our primary aim in the next lecture is to see how a diffraction pattern is related to this new concept of reciprocal space, and to understand the various experimental techniques involved in measuring diffraction patterns for crystal structure determination.

Appendix: Convolution theorem

We say that the function $f(x)$ is the convolution of two functions $g(x)$ and $h(x)$ if

$$f(x) = \int g(x')h(x - x') dx' \quad (11)$$

We denote this relationship as $f(x) = g(x) \otimes h(x)$ (an alternative representation sometimes used is $f = g * h$). The convolution is essentially an integral that expresses the amount of overlap of the function $h(x)$ as it is shifted over the function $g(x)$: it essentially “blends” one function with another.

The operation is commutative:

$$\begin{aligned} g(x) \otimes h(x) &= \int_{-\infty}^{\infty} g(x')h(x - x') dx' \\ &= \int_{\infty}^{-\infty} g(x - x'')h(x'') \cdot -dx'' \quad (x'' = x - x') \end{aligned} \quad (12)$$

$$= \int_{-\infty}^{\infty} h(x'')g(x - x'') dx'' \quad (13)$$

$$= h(x) \otimes g(x) \quad (14)$$

Our key result actually concerns the Fourier transform of a convolution. Writing the transforms of our three functions $f(x)$, $g(x)$ and $h(x)$ as $F(k)$, $G(k)$ and $H(k)$, respectively, we have:

$$F(k) = \int f(x) \exp(ikx) dx \quad (15)$$

$$= \int g(x) \otimes h(x) \exp(ikx) dx \quad (16)$$

$$= \iint g(x')h(x - x') \exp(ikx) dx' dx \quad (17)$$

$$= \iint g(x')h(x - x') \exp[ik(x - x')] \exp(ikx') dx' dx \quad (18)$$

$$= \int g(x') \exp(ikx') dx' \times \int h(x - x') \exp[ik(x - x')] dx \quad (19)$$

$$= \int g(x') \exp(ikx') dx' \times \int h(x'') \exp(ikx'') dx'' \quad (x'' = x - x') \quad (20)$$

$$= G(k) \times H(k) \quad (21)$$

Appendix: Reciprocal lattice derivation

Here we want to show that the Fourier transform of the one-dimensional lattice function $\mathcal{L}(x) = \sum_n \delta(x - na)$ is given by the reciprocal lattice function $\mathcal{R}(Q) = \sum_Q \delta(Q - 2\pi h/a)$. Let us define $\mathcal{R}(Q)$ as the Fourier transform of $\mathcal{L}(x)$. Then we have:

$$\mathcal{R}(Q) = \int \mathcal{L}(x) \exp(iQx) dx \quad (22)$$

$$= \int \sum_n \delta(x - na) \exp(iQx) dx \quad (23)$$

$$= \sum_n \int \delta(x - na) \exp(iQx) dx \quad (24)$$

Now, for each integral within the sum on the right-hand side of this equation we will partition space into two regions: that region such that x is less than a small distance ε from na , and all remaining values of x . That is,

$$\mathcal{R}(Q) = \sum_n \left[\int_{|x-na|=\varepsilon}^{\infty} \delta(x - na) \exp(iQx) dx \right. \\ \left. + \int_{|x-na|=0}^{|x-na|=\varepsilon} \delta(x - na) \exp(iQx) dx \right] \quad (25)$$

$$= \sum_n [0 + \exp(iQna)] \quad (26)$$

Now, for most Q , the summation on the right hand side will cancel over all values of n to give 0. The exception occurs whenever $Q = 2\pi h/a$ (h an integer), in which case

$$\mathcal{R}(Q) = \mathcal{R}(h) = \sum_n \exp(2\pi in h) \rightarrow \infty \quad (27)$$

So $\mathcal{R}(Q)$ is a series of spikes located at $Q = 2\pi h/a$; that is

$$\mathcal{R}(Q) = \sum_h \delta(Q - 2\pi h/a) \quad (28)$$

as required.

Extending this to three dimensions we have $\mathcal{L}(\mathbf{r}) = \sum_{UVW} \delta[\mathbf{r} - (U\mathbf{a} + V\mathbf{b} + W\mathbf{c})]$. Its Fourier transform is

$$\mathcal{R}(\mathbf{Q}) = \int \mathcal{L}(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \quad (29)$$

$$= \sum_{UVW} \exp[i\mathbf{Q} \cdot (U\mathbf{a} + V\mathbf{b} + W\mathbf{c})] \quad (30)$$

This function is now a three-dimensional set of δ -functions located at \mathbf{Q} for which $\mathbf{Q} \cdot (U\mathbf{a} + \mathbf{b} + \mathbf{c})$ is an integral multiple of 2π . Consider the vector

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad (31)$$

Note that $\mathbf{b} \times \mathbf{c}$ is a vector perpendicular to both \mathbf{b} and \mathbf{c} so that $\mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = 0$ and

$$\mathbf{a}^* \cdot \mathbf{a} = 2\pi \frac{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} = 2\pi \quad (32)$$

So $\mathbf{Q} = h\mathbf{a}^*$ will satisfy the δ -function requirement for all integral h . Similarly, assigning

$$\mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})} \quad (33)$$

and

$$\mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})} \quad (34)$$

means that any integral combination $\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ will also satisfy the requirements, giving

$$\mathcal{R}(\mathbf{Q}) = \sum_{hkl} \delta[\mathbf{Q} - (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)] \quad (35)$$

as required.