9 Brillouin zones

9.1 Diffraction

To resolve structural features at a length scale $d$, we need to image with light at wavelength $\lambda \leq d$. Solids have structural features given by the interatomic spacing, on the order of 2 Å. To probe the structure of solids, we need light with $\lambda \leq 2\text{Å}$, or x-rays. The periodicity of structures can be probed particularly effectively through diffraction: light waves reflected from the individual electrons can interfere constructively or destructively, and intense reflection is proof of constructive interference.

A visual aid, illustrated in Figure 1, is useful for understanding how and when diffraction occurs. Assume that we have light with wavelength $\lambda$, approaching the surface of a crystal at an angle $\theta$. If the atomic planes within the crystal are oriented to be parallel to the surface, there is an angle of approach $\theta$ with respect to the atomic planes, separated by a distance $d$, as well. Bragg made the assumption that planes of atoms in a crystal are partially reflective of light; to match observed x-ray penetration depths, some 0.5% of light must be reflected, and the remaining 99.5% is transmitted to the next atomic plane.

![Figure 1: Illustration of the Bragg condition: the path length difference of the two light waves $a$ and $b$, reflecting from "partially reflective" planes of atoms, is equal to an integer multiple of the wavelength $\lambda$.](http://magnet.ap.columbia.edu/msae4206/brillouin-zones.pdf)

If we consider that the light source is collimated, so that incoming waves $a$ and $b$ approach the partially reflective planes in parallel, the two waves are in phase until $b$ reaches the point indicated by the shaded triangle. Since the two waves share a common source, they must be in phase to begin. Similarly, exiting the crystal from the point defined by the second shaded triangle, $b$ acquires no phase difference with respect to $a$.

Any possible phase difference between the two waves occurs between the shaded triangles. The total path length difference $\delta$ acquired is $2d \sin \theta$. The
waves interfere constructively only if this distance $\delta$ is an integer multiple of the wavelength of light, or

$$n\lambda = 2d \sin \theta_B$$  \hspace{1cm} (1)

This is Bragg’s law. Bragg’s law is true, but its grounds are fictitious: light does not really reflect from atomic planes! Instead, each electron around an atom is accelerated by the $E$-field of the incident light, and the accelerated charge acts as a point-source for radiation. Constructive interference of these individual point sources is present, as it turns out, only in cases where the Bragg condition is met.

### 9.2 The scattering vector $q$

We can also define the Bragg condition vectorially. To do so, we need to introduce wave quantities $k, k', q$. There are two light waves to consider, one incident, with wavevector $k$, and one reflected, with wavevector $k'$. Remember, from the definition of the wavevector, we have $|k| = 2\pi/\lambda$. We define the scattering vector $q$ so that

$$k' = k + q$$ \hspace{1cm} (2)

$$k' - k = q$$ \hspace{1cm} (3)

Thus $q$ is the direction through which the light is scattered by the crystal.

The most typical geometry for diffraction experiments is symmetric, in which the surface normal and atomic plane normal are parallel to each other. This kind of diffraction experiment is often called a $\theta - 2\theta$ experiment, as illustrated in Figure 2. The x-ray source, which is usually bulky, tends to remain stationary; the sample and detector are mounted on two rotational
assemblies. In order to maintain $q$ normal to the surface, the sample rotates at an angle $\theta$, and the detector rotates at an angle $2\theta$. So while searching for a Bragg peak, the detector is rotated twice as quickly as the sample. This sort of fixed-wavelength experiment is usually preferred since a polychromatic x-ray sources are usually not available.

We can rewrite the Bragg condition as

$$k' - k = q_B$$

$$q_B = 2\pi G_{hkl}$$

where $q_B$ is the Bragg scattering vector, equal to $2\pi G_{hkl}$. $G_{hkl}$ is a reciprocal lattice vector, to be described. I will ask you to accept this condition for the moment; I will show how it is equivalent to Eq. 1 in Section 9.4.

9.3 The reciprocal lattice

The reciprocal lattice is essentially a map of the periodicity of the crystal, or a spatial Fourier transform. The periodicity of the crystal structure can be considered most cleanly by dividing the structure into a lattice and basis. (Fig 3)

The real lattice The crystal lattice is the repeat tiling of the atoms which comprise the crystal. The lattice posseses unit vectors $a_1$, $a_2$, and $a_3$, describing a parallelopiped; parallelopipded unit cells are stacked up in the unit vector directions to generate the crystal. The basis consists of the
atoms which reside inside the unit cell. The example given in Figure 3 is has a diatomic basis—two atoms per unit cell. Lattice vector translations \( T = m \mathbf{a}_1 + n \mathbf{a}_2 + i \mathbf{a}_3 \), \( m,n,o \) integers, connect identical environments within the crystal.

**Reciprocal lattice**  The *reciprocal lattice* \( \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3 \) is defined as:

\[
\begin{align*}
\mathbf{b}_1 & \equiv \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V} \\
\mathbf{b}_2 & \equiv \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V} \\
\mathbf{b}_3 & \equiv \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V}
\end{align*}
\]  

(6)  
(7)  
(8)

where the volume of the (real) unit cell \( V \) is

\[
V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)
\]  

(9)

remembering the standard formula for the volume of a parallelopiped.

Reciprocal lattice vectors are defined as \( \mathbf{G}_{hkl} = h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3 \), \( h,k,l \) integers; these connect points on the reciprocal lattice. One can verify immediately that

\[
\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{i,j}
\]  

(10)

where \( \delta_{i,j} \) is the Kronecker delta, \( \delta_{i,j} = 0 \) for \( i \neq j \) and \( \delta_{i,j} = 1 \) for \( i = j \).

There are two features of the reciprocal lattice which make it an interesting construction.

1. **\( \mathbf{G}_{hkl} \) is perpendicular to the plane (hkl).** The Miller index plane \( (hkl) \) makes intercepts of 1/h, 1/k, and 1/l on the \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) axes respectively. For a cubic system, \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) lie along the coordinate axes \( \hat{x}, \hat{y}, \hat{z} \), so the (100) plane, for example, is parallel to the \( y \) and \( z \) axes, making intercepts at \( y = \infty, z = \infty \).

To show that a vector is perpendicular to a plane, we need only show that the vector is perpendicular to two vectors which lie in the plane. For the plane \( (hkl) \) as described, two vectors are then \( \mathbf{u}_1 = 1/h \mathbf{a}_1 - 1/k \mathbf{a}_2 \) and \( \mathbf{u}_2 = 1/k \mathbf{a}_2 - 1/l \mathbf{a}_3 \). We just need to show \( \mathbf{u}_1 \cdot \mathbf{G}_{hkl} = 0 \) and \( \mathbf{u}_2 \cdot \mathbf{G}_{hkl} = 0 \) We then have

\[
\mathbf{u}_1 \cdot \mathbf{G}_{hkl} = (\frac{1}{h} \mathbf{a}_1 - \frac{1}{k} \mathbf{a}_2) \cdot (h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3) = 1 - 1 = 0
\]  

(11)
and similarly

\[ u_2 \cdot G_{hkl} = (\frac{1}{k} a_2 - \frac{1}{l} a_3) \cdot (h b_1 + k b_2 + l b_3) = 1 - 1 = 0 \]  \hspace{1cm} (12)

2. The magnitude of \( G_{hkl} \) is equal to the reciprocal distance between the planes \((hkl)\), or \( |G_{hkl}| = 1/d_{hkl} \). To verify, we know that the interplane spacing \( d_{hkl} \) must be equal to the component of any coordinate axis distance to the plane, e.g. \( a_1/h \), taken along the plane unit normal \( \mathbf{n} \):

\[ d_{hkl} = \frac{a_1}{h} \cdot \mathbf{n} = \frac{a_1}{h} \cdot (h b_1 + k b_2 + l b_3) = 1/|G_{hkl}| \]  \hspace{1cm} (13)

An illustration of the reciprocal lattice for the 2-D oblique surface net is shown in Figure 4. It can be seen that the direction of the \((01)\) spot, pointing from \((00)\), for example, is perpendicular to the planes running diagonally in the real-space lattice, illustrating rule #1. Similarly, \( b_2 \) is longer than \( b_1 \) since the horizontal planes are more closely packed, illustrating rule #2.

9.4 The Ewald sphere

The Bragg condition

\[ k' - k = q_B = 2\pi G_{hkl} \]  \hspace{1cm} (14)

can be understood graphically using a construction known as the Ewald sphere. This construction relies on the fact that we are usually interested in
elastic light scattering, so energies and $\lambda$ are the same for $\mathbf{k}$ and $\mathbf{k}'$, and from $k = 2\pi/\lambda$, $|k| = |k'|$. So, if we orient $\mathbf{k}$ so that it takes its actual propagation direction with respect to the lattice, the set of all possible arbitrary scattering vectors $\mathbf{k}'$ lie on a sphere, if we place $\mathbf{k}$ and $\mathbf{k}'$ tail-to-tail.

We conventionally place $\mathbf{k}/2\pi$ so that it terminates on the $G_{0,0,0}$ spot of the reciprocal lattice. If some $G_{hkl}$ intersects the Ewald sphere, then the Bragg condition is satisfied for that $G_{hkl}$ reflection.\(^1\) To see this diffracted beam, we have to position our detector to intersect with $\mathbf{k}'$ (see Figure 2).

In Figure 5, we show the diffraction condition satisfied for the (13) reflection of the oblique surface net. (This scattering vector would have to be in the 2D plane of the lattice.) One can see how the scattering vector $\mathbf{q}$ acts as a "searchlight" for diffraction: if $\mathbf{q}$ lands on some $G_{hkl}$, the diffraction condition is satisfied. One can see at the same time that the (12) reflection is satisfied, so diffracted radiation is exiting the crystal at a $\mathbf{k}'$ defined by termination on this spot as well. However, it would not be observed unless we have a position-sensitive (non-symmetric) detector capable of resolving several $\mathbf{k}'$ simultaneously, or if we reposition the detector to intersect this diffracted beam.

\(^1\)The choice of $\mathbf{k}$ termination point is unimportant, since the reciprocal lattice is a lattice, and a [13] vector will connect two points on the reciprocal lattice regardless of where the first point sits.
Reduction to Bragg’s law : How does this condition reduce to the simple law written in Eq. 1? Taking the dot product of both sides with $\mathbf{k}$, referring to Figure 5, and remembering that $\mathbf{a} \cdot \mathbf{b} = |a||b| \cos \theta$, we have

\begin{align*}
\frac{1}{2\pi}(k' - k) &= G_{hkl} \\
\frac{1}{2\pi}(k \cdot k' - k \cdot k) &= k \cdot G_{hkl} \\
\frac{1}{2\pi} \left( \frac{2\pi}{\lambda} \right)^2 (\cos 2\theta - 1) &= -\frac{2\pi}{\lambda} \left( \frac{1}{d_{hkl}} \right) \cos \left( \frac{\pi}{2} - \theta \right) \\
-\frac{1}{\lambda} \sin^2 \theta &= \frac{1}{d_{hkl}} \sin \theta \\
\lambda &= 2d_{hkl} \sin \theta
\end{align*}

(15) (16) (17) (18) (19)

9.5 Brillouin zones

Zone boundary condition for diffraction There is an additional way to state the Bragg condition, leading to a natural presentation of all possible waves in a crystal. Rewriting Bragg as

\begin{align*}
\mathbf{k} + 2\pi \mathbf{G} &= \mathbf{k}' \\
|\mathbf{k} + 2\pi \mathbf{G}|^2 &= |\mathbf{k}'|^2 \\
(\mathbf{k} + 2\pi \mathbf{G}) \cdot (\mathbf{k} + 2\pi \mathbf{G}) &= |\mathbf{k}'|^2 \\
|\mathbf{k}|^2 + 4\pi \mathbf{k} \cdot \mathbf{G} + (2\pi)^2 |\mathbf{G}|^2 &= |\mathbf{k}'|^2 \\
\mathbf{k} \cdot \mathbf{G} &= \frac{1}{2} (2\pi) |\mathbf{G}|^2 \\
\mathbf{k} \cdot \frac{\mathbf{G}}{2} &= (2\pi) \frac{|\mathbf{G}|^2}{2}
\end{align*}

(20) (21) (22) (23) (24) (25)

we can see that any incident wave $\mathbf{k}/2\pi$ with a component along a reciprocal lattice vector $\mathbf{G}$ equal to half that reciprocal lattice vector is diffracted. This condition is easier to see illustrated than to appreciate mathematically. Any incident wavevector $\mathbf{k}$ which touches the perpendicular bisector between $\mathbf{G}_{000}$ and $\mathbf{G}_{hkl}$ is diffracted. See Figure 6 for an illustration of the zone boundaries in the oblique surface net.

Brillouin Zones We can define a geometrical shape, the Brillouin Zone, based on the position of these zone boundaries. The Brillouin Zone is defined
Figure 6: Illustration of diffraction occurring at Brillouin zone boundaries, according to condition 25. Waves \( k_1 \) and \( k_2 \), which meet the zone boundaries of (perpendicular bisector to) \( G_{10} \) are diffracted by (10) reflections; wave \( k_3 \) is diffracted by the \((11)\) reflection.

as the Wigner-Seitz cell in reciprocal space. The Wigner-Seitz cell is defined as the smallest polyhedron enclosed by the perpendicular bisectors of the nearest neighbors to a lattice point. The Brillouin Zone is the Wigner-Seitz cell in reciprocal space. First, second, third, and fourth Brillouin Zones (BZ) are defined as the smallest, second-smallest, third-smallest, and fourth-smallest polyhedra enclosed by bisecting planes. These constructions are illustrated in Figure 7.

Why is this useful? You can verify by inspection that all of reciprocal space can be filled by repeated placement of the first BZ on each reciprocal lattice point. We will show soon that if \( k \) represents not an x-ray but an electron-wave in the crystal, any \( k \) is equivalent to \( k + G_{hkl} \), where \( G_{hkl} \) is any reciprocal lattice point. So if we would like to consider all possible electronic states in the crystal, we need to only look in the first BZ. States in the second and higher-order BZ’s can be reduced to the first BZ with no loss of generality.
Figure 7: Left: First Brillouin zone for the oblique 2D surface net. To form the Wigner-Seitz cell for this reciprocal lattice, it is necessary to go out to the boundaries to the third nearest neighbor (marked 1-3). Right: Brillouin zones for the 2D square lattice. The first, second, third, and fourth Brillouin zones are marked by ascending darkness in shading; only first and second (1,2) nearest neighbors need to be considered in this case.