Digression: Estimate atom density of a solid

Exercise

How many Si atoms (both types A & B) are in the conventional unit cell?

What is the atom density of Si (in atoms/cm³)?

**Solution 1:** Use lattice parameter $a = 0.543$ nm to calculate the volume of the conventional unit cell. Count how many Si atoms there are in the conventional unit cell. Divide this number by the volume. Convert to atoms /cm³.

**Solution 2:** There are $\sim 6 \times 10^{23}$ atoms in 1 mole of Si (Avogadro constant). Si is the # 14 element $\Rightarrow$ the atomic mass is $\sim 28$ g/mol. The density of water is $\sim 1$ g/cm³ = 1 kg/l = 1 ton/m³. Typical solids are on the same order of magnitude or one order of magnitude denser.

Let the density of Si be $\rho$. The volume of 1 mol (i.e. 28 g) of Si is

$$\frac{28 \text{ g}}{\rho \text{ g/cm}^3} = \frac{28}{\rho} \text{ cm}^3.$$ 

The denominator is on the order of $10^0$ but $> 1$. For a rough estimate, let’s say this volume is $\sim 10$ cm³. Therefore, the atom density is $\sim 6 \times 10^{23}$ atoms / 10 cm³ = $6 \times 10^{22}$ atoms/cm³.

To be more accurate, we can use $\rho = 2.3$ g/cm³ to calculate the volume of 1 mol Si:

$$\frac{28}{\rho} \text{ cm}^3 = \frac{28}{2.3} \text{ cm}^3 \approx 12 \text{ cm}^3.$$ 

Thus, the Si atom density is $6 \times 10^{23}$ atoms / 12 cm³ = $5 \times 10^{22}$ atoms/cm³.
## Atom densities of semiconductors

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Ge</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>14</td>
<td>32</td>
<td>31 for Ga, 33 for As</td>
</tr>
<tr>
<td>Atomic mass (g/mol)</td>
<td>28.1</td>
<td>72.6</td>
<td>69.7 for Ga, 74.9 for As</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.3</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Atom density ($10^{22}$/cm³)</td>
<td>5.0</td>
<td>4.4</td>
<td>4.4 (Ga and As total)</td>
</tr>
<tr>
<td>Lattice constant (nm)</td>
<td>0.543</td>
<td>0.565</td>
<td>0.565</td>
</tr>
</tbody>
</table>
Reciprocal lattice

Crystal structure (real space) recap

A crystal is a **periodic** structure.

A period of the crystal structure is a **unit cell**, having an internal structure.

An integer multiple of a period is also a period.

The smallest possible period is called a **primitive unit cell**.

A **conventional unit cell** is often used to better visualize features of a crystal structure.

The underlying periodic lattice of a crystal structure without unit cell internal structure is the **Bravais lattice**.

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Si crystal structure

[Image of Si crystal structure]

http://www.webelements.com/silicon/crystal_structure.html

Conventional unit cell

[Image of conventional unit cell]

Primitive unit cell

[Image of primitive unit cell]

http://onlineheavytheory.net/silicon.html

Electrons viewed as plane waves diffracted by the crystal structure as a 3D lattice/grating.

**1D example**: the unit cell can have an internal structure

![Diagram of 1D unit cell with A and B atoms]

Polyacetylene:

![Polyacetylene structure]

Diffraction is Nature’s way of doing Fourier transform:

![Diagram of diffraction pattern]

To have constructive interference between reflections by the same atoms (e.g. A) of all unit cells: consider the periodicity of the *Bravais lattice*

\[ a = \frac{\lambda}{2n} \]
Diffraction is Nature’s way of doing Fourier transform.

\[ a = \frac{\lambda}{2n} \quad \text{or} \quad \frac{2\pi}{k} = \lambda = \frac{2a}{n} \quad \Rightarrow \quad k = n \frac{2\pi}{2a} \]

Bragg condition for constructive interference:

The change in \( k \) (wave vector) upon reflection is

\[ |\Delta k| = |k_f - k_i| = 2 \left( n \frac{2\pi}{2a} \right) = n \frac{2\pi}{a} \]

You see, the Fourier transform is just a “spectrum” of \( \Delta k \).
This is just like the Fourier transformation of time domain signals:

\[ \omega_0 = \frac{2\pi}{T} \]

(We just renamed \( \Delta k \) as \( G \))
Fourier transform in 2D: Each family of lines has a corresponding Bragg condition

\[ |\Delta k| = n \frac{2\pi}{d} \]

\( d = b \uparrow \)

\( d = a \)
Each reciprocal lattice vector (point) and its integer multiples correspond to one family of parallel lines of real lattice points.
In 3D, each reciprocal lattice vector (point) and its integer multiples correspond to one family of parallel planes of real lattice points.
Mathematical formalism of Bravais lattices and the reciprocal space

1D: Each lattice point is represented by a “vector” \( R = na \), where \( n \) is an integer. The lattice remains the same upon translation by \( R \).

The reciprocal lattice vectors are \( G = mb \), where \( m \) is an integer and \( b = 2\pi/a \).

\[ GR = 2\pi(mn) \]

Alternative notations/conventions: \( a^* \to b \), \( K \to G \)
2D: Each lattice point is represented by a vector \( \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \), where \( n_1 \) and \( n_2 \) are integers. The lattice remains unchanged upon translation by \( \mathbf{R} \).

The reciprocal lattice vectors are \( \mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 \), where \( m_1 \) and \( m_2 \) are integers.

\[
\begin{align*}
\mathbf{b}_1 &= \frac{2\pi \mathbf{a}_2 \times \hat{n}}{|\mathbf{a}_1 \times \mathbf{a}_2|} \\
\mathbf{b}_2 &= \frac{2\pi \hat{n} \times \mathbf{a}_1}{|\mathbf{a}_1 \times \mathbf{a}_2|}
\end{align*}
\]

\[
\begin{align*}
\mathbf{a}_1 \cdot \mathbf{b}_1 &= 2\pi \\
\mathbf{a}_2 \cdot \mathbf{b}_2 &= 2\pi
\end{align*}
\]

\[ \Rightarrow \quad \mathbf{G} \cdot \mathbf{R} = 2\pi (m_1 n_1 + m_2 n_2) \]

\( \hat{n} \): normal unit vector of 2D lattice

Area of the real-space lattice primitive unit cell is \( |\mathbf{a}_1 \times \mathbf{a}_2| \). Area of reciprocal lattice unit cell is \( 4\pi^2 / |\mathbf{a}_1 \times \mathbf{a}_2| \).

Notice that \( \mathbf{b}_1 \perp \mathbf{a}_2 \) and \( \mathbf{b}_2 \perp \mathbf{a}_1 \), but the following are not always true:

\( \mathbf{b}_1 \parallel \mathbf{a}_1, \mathbf{b}_2 \parallel \mathbf{a}_2 \)

Alternative notations/conventions:

- \( \mathbf{a} \rightarrow \mathbf{a}_1, \mathbf{b} \rightarrow \mathbf{a}_2 \);
- \( \mathbf{a}^* \rightarrow \mathbf{b}_1, \mathbf{b}^* \rightarrow \mathbf{b}_2 \);
- \( K \rightarrow G \)
One more example: the 2D triangular lattice

Here, the following are not true: \( \mathbf{b}_1 \parallel \mathbf{a}_1, \mathbf{b}_2 \parallel \mathbf{a}_2 \)
3D: Each lattice point is represented by a vector \( \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \), where \( n_1, n_2, \) and \( n_3 \) are integers. The lattice remains unchanged upon translation by \( \mathbf{R} \).

The reciprocal lattice vectors are \( \mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \), where \( m_1, m_2, \) and \( m_3 \) are integers.

\[
\begin{align*}
\mathbf{b}_1 &= \frac{2 \pi \mathbf{a}_2 \times \mathbf{a}_3}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3} \\
\mathbf{b}_2 &= \frac{2 \pi \mathbf{a}_3 \times \mathbf{a}_1}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3} \\
\mathbf{b}_3 &= \frac{2 \pi \mathbf{a}_1 \times \mathbf{a}_2}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3}
\end{align*}
\]

\[
\begin{align*}
\mathbf{a}_1 \cdot \mathbf{b}_1 &= 2 \pi \\
\mathbf{a}_2 \cdot \mathbf{b}_2 &= 2 \pi \\
\mathbf{a}_3 \cdot \mathbf{b}_3 &= 2 \pi 
\end{align*}
\]

\( \Rightarrow \mathbf{G} \cdot \mathbf{R} = 2 \pi (m_1 n_1 + m_2 n_2 + m_3 n_3) \)

Area of the real-space lattice primitive unit cell is \( V_p = (\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3 \).

Area of reciprocal lattice unit cell is \( 8 \pi^3 / V_p \).

Notice that \( \mathbf{b}_1 \perp \mathbf{a}_2 \) and \( \mathbf{b}_2 \perp \mathbf{a}_1 \), but the following are not always true: \( \mathbf{b}_1 \parallel \mathbf{a}_1, \mathbf{b}_2 \parallel \mathbf{a}_2 \)

Alternative notations/conventions:

\( a \rightarrow \mathbf{a}_1, b \rightarrow \mathbf{a}_2, c \rightarrow \mathbf{a}_3; a^* \rightarrow \mathbf{b}_1, b^* \rightarrow \mathbf{b}_2, c^* \rightarrow \mathbf{b}_3; K \rightarrow \mathbf{G} \)
In solid-state physics, we use $G$ or $K$ as “spatial (angular) frequency” of the real-space lattice; they are the spatial equivalent of angular frequency $\omega$.

Many research tools (instruments e.g. TEM, image processing software e.g. FFT) instead use the “spatial frequency”, i.e., the spatial equivalent of frequency $f$.

The two differ by a factor $2\pi$. 
We will use “aliasing” as analogy to explain electron waves in crystals. This is not rigorous, but heuristic. (“No analogy is complete.”)

“Aliasing” in signals and systems

Frequency $f + f_s$, where $f_s = 1/T_s$ is sampling rate.

Frequency $f$

Sampling pulse train

Fourier transformation

$\omega_s = 2\pi/T_s$

$0$
Signals of frequencies $f + nf_s$ are not distinguishable. Therefore, we only need to keep one of the replica, usually the one from $-f_s/2$ to $f_s/2$.

Similarly, electron waves of wave vectors $k$ and $k + K$ (where $K = n(2\pi/a)$ are reciprocal lattice vectors) are indistinguishable in a periodic crystal structure.

In this course, we state this point as a conclusion without proof; it is the consequence of Block theorem. The electronic states in a periodic crystal structure are called Bloch states.
Signals of frequencies $f + nf_s$ are indistinguishable. Therefore, we only need to keep one of the replica in any spectral range that is $f_s$ wide. Usually, we filter out all other replicas and keep the one from $-f_s/2$ to $f_s/2$.

Similarly, electron waves of wave vectors $k$ and $k + K$ (where $K = n(2\pi/a)$ are reciprocal lattice vectors) are indistinguishable in a periodic crystal structure.

Block states in any range of $k$ that is $2\pi/a$ wide are complete. Therefore, we can describe electrons with Bloch states in any one of such ranges. Such a $2\pi/a$ wide region in the reciprocal space is called a Brillouin zone (BZ). A Brillouin zone is a primitive unit cell of the reciprocal space. The Brillouin zone from $-2\pi/a$ to $2\pi/a$ is called the first Brillouin zone (1st BZ) or simply BZ.
First, we consider **free electrons** (potential energy = 0; all energy is kinetic). Recall that $p = h/\lambda = h k / (2\pi) = \hbar k$ and $E = p^2 / 2m$.

$$\Rightarrow \quad E = \hbar^2 k^2 / 2m$$

The free electrons are scattered (or diffracted) by a grating represented by “spatial (angular) frequencies” $K$.

Electron waves of wave vectors $k$ and $k + K$ are indistinguishable due to the interaction, as if the lattice can impart momenta $K$ to the electron without causing any change.

Yu & Cardona, Section 2.2, p. 21.
Bloch states labeled wave by vector \( k \) and wave vector \( k + K \) are indistinguishable. Thus, we can shift segments of the \( E(k) \) dispersion curve outside the 1\(^{st} \) BZ into it.

Fig. 2.1. The band structure of a free particle shown in (a) the extended zone scheme and (b) the reduced zone scheme.

Shift segments of \( E(k) \) dispersion curve into the 1\(^{st} \) Brillouin zone, i.e., \((- \pi / a, \pi / a]\).

Points \( k = \pm \pi / a \) in reciprocal space are called zone boundaries.
Far away from zone boundaries, different Bloch states specified by the same $k$ are far away from each other in energy, i.e., the states are far from resonance. $E(k)$ curve similar to free e.

Around zone boundaries and zone center ($k = 0$), states of similar $k$ (i.e. similar $\lambda$) are close to each other in energy, therefore they interfere with each other, giving rise to standing waves. In other words, they are resonant.

Due to standing waves, a wave similar to free e cannot propagate. Energies corresponding to free e at those $k$ are not allowed.

The prohibited energy ranges are gaps, and the allowed ranges are bands.
Motion of Bloch electrons

An electron is a wave packet.

A wave packet is the superposition of plane waves in a small range of $k$.

The narrower the wave packet, the wider its $k$ range (just as the narrower a pulse the broader its spectrum), and vice versa: $\Delta x \Delta k \sim 1$.

Since momentum $p = \hbar k$, $\Delta x \Delta p \sim \hbar$. This is the famous principle of uncertainty.

The velocity of the electron is the velocity of the wave packet.

As for any wave, a wave packet (the envelope) moves at the group velocity

$$\frac{d\omega}{dk} \equiv v_g.$$ 

$$E = \hbar \omega$$

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$$

First, we consider the free electron. $E = \hbar^2 k^2 / 2m$

$$v_g = \frac{1}{\hbar} \frac{dE}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v$$

Next, we use the free e analogy to build a semi-classical theory for Bloch electrons.
In our “nearly free electron” model, $E = \frac{\hbar^2 k^2}{2m}$ at the bottom of lowest band.

Bottom of each of other bands can be expressed as $E \propto k^2$ (Taylor expansion). Therefore, we can write

$$E = \frac{\hbar^2 k^2}{2m^*}$$

Next, we show that the effective mass can be defined more generally.
At the bottom of a band, 

\[ E = \frac{\hbar^2 k^2}{2m^*} = \frac{p^2}{2m^*} \]

It appears that we can describe the Bloch e as a classical e with a modified mass, \( m^* \).

Let’s give it a try. Let’s try to make the Bloch e follow Newton’s 2nd law:

**Externally applied** force, not due to ion cores or other electrons in crystal

\[ F = m^* a = m^* \frac{dv}{dt} = \frac{dp}{dt} \]

\[ v = \frac{1}{\hbar} \frac{dE}{dk} \]

\[ \Rightarrow \quad \frac{1}{m^*} = \frac{dv}{dp} = \frac{1}{\hbar} \frac{dv}{dk} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \]

So, the effective mass is just (proportional to) the reciprocal of the second derivative (or “curvature”) of the \( E(k) \) dispersion curve.

**Summary of the 1D semi-classical model**

Electron moves at the group velocity. \( v = \frac{1}{\hbar} \frac{dE}{dk} \)

Electron behaves as a classical e with mass \( m^* \).

In general, \( m^* \) is a function of \( k \).

With this, electron follows Newton’s laws. \( E = \frac{\hbar^2 k^2}{2m^*} = \frac{p^2}{2m^*} \)

The forces by the ion cores and other electrons are accounted for by the modified mass. **Only** applied forces enter Newton’s 2nd law.

\[ F = m^* \frac{dv}{dt} = \frac{dp}{dt} = \hbar \frac{dk}{dt} \]