A Concise Summary of Solid State Physics

Condensed notes of the material covered in the third-year undergraduate course *Fizika trdne snovi* (Solid State Physics) at the Faculty of Mathematics and Physics at the University of Ljubljana in the academic year 2020-21. The course covers solid state physics at an upper-undergraduate level and draws heavily from Ashcroft and Mermin's *Solid State Physics*.

Disclaimer: This document will inevitably contain some mistakes—both simple typos and legitimate errors. Keep in mind that these are the notes of an undergraduate student in the process of learning the material himself, so take what you read with a grain of salt. If you find mistakes and feel like telling me, I will be grateful and happy to hear from you, even for the most trivial of errors. You can reach me by email, in English, Slovene, or Spanish, at `ejmastnak@gmail.com`.

Elijan J. Mastnak
Last update: October 10, 2022
Faculty of Mathematics and Physics, University of Ljubljana

Contents

Crystal Structure

Crystals are solid-state materials whose microscopic building blocks (e.g. atoms, molecules, ions, etc...) are arranged in a well-defined, highly-ordered geometric structure.
Crystal structure is analyzed in terms of *Bravais lattices*.

Bravais Lattice
A Bravais lattice Λ is a set of points $\{\mathbf{R}\} \subset \mathbb{R}^3$ given by
$\Lambda \equiv \left\{ \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \mid n_i \in \mathbb{Z} \right\}$, where $n_1, n_2, n_3 \in \mathbb{Z}$ are arbitrary integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are linearly independent vectors, called *primitive vectors*, spanning the Bravais lattice.

- A set of primitive vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ specifies a unique Bravais lattice. However, the choice of $\{\mathbf{a}_i\}$ used to describe a given Bravais lattice is not unique.

- A Bravais lattice appears identical when viewed from any lattice point for any fixed viewing direction.

- A Bravais lattice is a discrete set of non-coplanar vectors closed under addition and subtraction.

A Bravais lattice's *coordination number* is the number of lattice sites closer to any given lattice site $\mathbf{R}_0$ than to any other point in the lattice (the number of nearest neighbor sites any point in the lattice has).

Primitive Unit Cell
The smallest region of space that repeats periodically throughout a crystal is called a *primitive unit cell*.
The positions of a crystal's PUCs are given by a Bravais lattice.
$\Lambda = \left\{ \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \right\}$ (positions of PUCs)
Mathematical definition: the crystal's PUC is the smallest region of space the tesselates the ambient space $\mathbb{R}^3$ when translated by linear combinations of the primitive vectors $\mathbf{a}_i$.

Basis
The positions of physical atoms within each PUC are given by a *basis*—a set of vectors $\{\mathbf{d}_j\}$ given the positions of atoms in the PUC relative to the lattice site.
A crystal with M atoms per PUC has M basis vectors $\{\mathbf{d}_j\}_{j=1}^M$
The positions of atoms forming a crystal are specified with a Bravais lattice together with a basis at each lattice point.
$\mathbf{r}_\mathbf{n}^{(j)} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 + \mathbf{d}_j$ (position of atoms)
(for $\mathbf{n} = (n_1, n_2, n_3)$)

Primitive Unit Cell Properties
Consider a crystal whose PUC positions are given by the BL
$\Lambda = \left\{ \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \right\}$

- PUCs contain exactly on lattice point

- The configuration of atoms is identical in every PUC

- All PUCs have the same volume V_0

$V_0 = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ (volume of a PUC)
Interpretation: V_0 is the volume of the parallelepiped spanned by the Bravais lattice's primitive vectors $\{\mathbf{a}_i\}$.

Parallelepiped Unit Cell
The parallelepiped unit cell is the region of space spanned by a BL's primitive vectors and specified mathematically as the region $\Omega_{\mathrm{pp}} \subset \mathbb{R}^3$ given by...
$\Omega_{\mathrm{pp}} \equiv \left\{ \mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3; \ x_i \in [0, 1) \right\}$

Conventional Unit Cell
The conventional unit cell is constructed to display lattice's full symmetry properties. The CUC is generally larger than a primitive unit cell with volume equal to an integer multiple of PUC volume V_0.

Wigner-Seitz Unit Cell
The Wigner-Seitz unit cell is the set of all points in space closer to any fixed lattice site in a Bravais lattice than to any other lattice site.
Mathematically, the WS cell is the region $\Omega_{\mathrm{WS}} \subset \mathbb{R}^3$ given by
$\Omega_{\mathrm{WS}} \equiv \left\{ \mathbf{r} \in \mathbb{R}^3 \colon |\mathbf{r}| < |\mathbf{r} - \mathbf{R}| \text{ for all } \mathbf{R} \in \Lambda \right\}$
(assuming the origin coincides with a lattice site)
Construction:

1. Choose a lattice point in the BL as the origin

2. Draw lines connecting origin to all nearest-neighbor lattice sites

3. Draw perpendicularly bisecting planes through above lines. The Wigner-Seitz PUC is region bounded by the bisecting planes

The Wigner-Seitz cell preserves the lattice's full set of point symmetries.

Symmetries of a Bravais Lattice

Translation Symmetry
Consider a Bravais lattice with primitive vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$
$\mathbf{T}_\mathbf{n} = n_1\mathbf{v}_1 + n_2\mathbf{v}_2 + n_3\mathbf{v}_3$ (general translation operator)
$\mathbf{v}_i \in \mathbb{R}^3$ are arbitrary vectors
$\mathbf{n} = (n_1, n_2, n_3)$ where $n_1, n_2, n_3 \in \mathbb{Z}$
$\mathbf{T}_\mathbf{n}$ represents a translation of the Bravais lattice's origin from the original position $\mathbf{r} = \mathbf{0}$ the new position $\mathbf{r}' = n_i\mathbf{v}_i$
Bravais lattices are invariant under translations by the primitive vectors, i.e. under translations of the form...
$\mathbf{T}_\mathbf{n} = n_1 + \mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ (BL invariant if $\{\mathbf{v}_i\} = \{\mathbf{a}_i\}$)

Point Symmetries
At least on point in the lattice remains in the same position after a point operation
Examples include:

- Rotation

- Reflection

- Inversion

- Improper rotation (rotation with reflection)

Rotation: an n-fold rotation is rotation that maps a lattice back into its original position when repeated n times.
The angle of an n-fold rotation is $\theta_n = 2\pi/n$.

Examples of Bravais Lattices

Simple Cubic (SC)
The conventional (and primitive) unit cell is a cube with side lengths a and lattice sites at each cube vertex.
Wigner-Seitz cell is a cube centered on a lattice site
Example: Polonium
$N_\mathrm{c} = 6$ (coordination number)
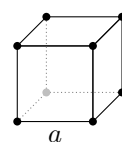
$\mathbf{a}_1 = a\,\hat{\mathbf{x}}$
$\mathbf{a}_2 = a\,\hat{\mathbf{y}}$
$\mathbf{a}_3 = a\,\hat{\mathbf{z}}$

Body-Centered Cubic (BCC)
The conventional unit cell is a cube with side lengths a.
Lattice sites occur at each cube vertex and at cube center

Wigner-Seitz cell is a truncated octahedron
Examples: Ba, Cr, Cs, Fe, K
$N_c = 8$ (coordination number)

$$\mathbf{a}_1 = a\,\hat{\mathbf{x}} \qquad \mathbf{a}_1 = \tfrac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$$
$$\mathbf{a}_2 = a\,\hat{\mathbf{y}} \qquad \mathbf{a}_2 = \tfrac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}})$$
$$\mathbf{a}_3 = \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \qquad \mathbf{a}_3 = \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

Face-Centered Cubic (FCC)
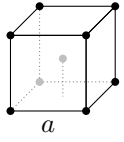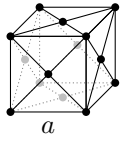The conventional unit cell is a cube with side lengths a.
Lattice sites occur at each cube vertex and at the center of each cube face
Wigner-Seitz cell is a rhombic dodecahedron
Examples: Ar, Ag, Au, Ca, Ce
$N_c = 12$ (coordination number)

$$\mathbf{a}_1 = \tfrac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$
$$\mathbf{a}_2 = \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$$
$$\mathbf{a}_3 = \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

Diamond Structure
Structure: two FCC lattice superimposed on each other, with one shifted relative to the other along the main body diagonal by one fourth of the body diagonal length.
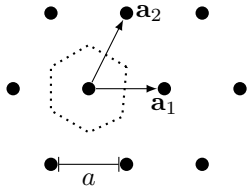Formulation: FCC primitive vectors plus the basis $\mathbf{d}_1 = \mathbf{0}$ and $\mathbf{d}_2 = \tfrac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$
The diamond structure is not a Bravais lattice!

2D Hexagonal (aka Triangular) Lattice
Lattice sites are arranged in a hexagonal pattern
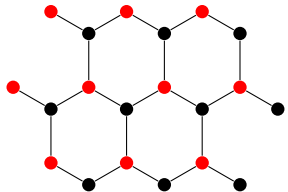The Wigner-Seitz cell is a hexagon of side length $a/\sqrt{3}$ centered on a lattice site

$$\mathbf{a}_1 = a\,\hat{\mathbf{x}}$$
$$\mathbf{a}_2 = \tfrac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\,\hat{\mathbf{y}})$$

The Honeycomb Structure
Structure: Two hexagonal lattice sites superimposed on each other, one shifted relative to the other by $\tfrac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\,\hat{\mathbf{y}}/3)$.
The honeycomb structure is not a Bravais lattice!
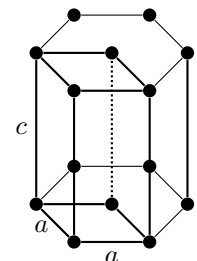

$$\mathbf{a}_1 = a\,\hat{\mathbf{x}}$$
$$\mathbf{a}_2 = \tfrac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\,\hat{\mathbf{y}})$$
$$\mathbf{d}_1 = \hat{\mathbf{0}}$$
$$\mathbf{d}_2 = \tfrac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\,\hat{\mathbf{y}}/3)$$

3D Hexagonal Lattice
Structure: two 2D hexagonal lattices superimposed on each other and separated along the $\hat{\mathbf{z}}$ axis by the distance c.

$$\mathbf{a}_1 = a\,\hat{\mathbf{x}}$$
$$\mathbf{a}_2 = \tfrac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\,\hat{\mathbf{y}})$$
$$\mathbf{a}_3 = c\,\hat{\mathbf{z}}$$

Reciprocal Lattice
A reciprocal lattice is defined only in the context of a Bravais lattice. Consider a BL Λ spanned by primitive vectors $\{\mathbf{a}_i\}$.
The BL's *reciprocal lattice* Λ^* is the set of all $\mathbf{K}$ such that...
$e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for all $\mathbf{R} \in \Lambda$ (RL condition)
$\Lambda^* \equiv \left\{ \mathbf{K} \mid e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda \right\}$ (definition of RL)

Interpretation of the Reciprocal Lattice
Consider a Bravais lattice Λ with lattice sites $\mathbf{R}$.
The BL's reciprocal lattice is the set of $\mathbf{K}$ for which the general plane wave $e^{i\mathbf{K}\cdot\mathbf{r}}$ has the periodicity of the BL, i.e....
$e^{i\mathbf{K}\cdot(\mathbf{R}+\mathbf{r})} = e^{i\mathbf{K}\cdot\mathbf{r}}$ for all $\mathbf{r} \in \mathbb{R}^3$ and $\mathbf{R} \in \Lambda$
$\implies e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for all $\mathbf{R} \in \Lambda$ (recovers RL condition)

Reciprocal Primitive Vectors
Consider a Bravais lattice Λ spanned by primitive vectors $\{\mathbf{a}_i\}$
$\Lambda^* \equiv \left\{ \mathbf{K} \mid e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda \right\}$ (reciprocal lattice)
The reciprocal lattice vectors may be written in the form...
$\mathbf{K} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$
$m_1, m_2, m_3 \in \mathbb{Z}$ are arbitrary integers
$\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are *reciprocal primitive vectors*
$V_0 = |\mathbf{a}_1 \times (\mathbf{a}_2 \times \mathbf{a}_3)|$ (review: volume of BL's PUC)

The RL's *reciprocal primitive vectors* $\{\mathbf{b}_i\}$ are given by...
$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ (**implicit definition of reciprocal PV**)
$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_0}$ (RPV in terms of PV)
$\mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_0}$ (RPV in terms of PV)
$\mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_0}$ (RPV in terms of PV)

The BL's PVs $\{\mathbf{a}_i\}$ are given in terms of $\{\mathbf{b}_i\}$ by...
$\mathbf{a}_1 = 2\pi\frac{\mathbf{b}_2 \times \mathbf{b}_3}{V_0^*}$ (PV in terms of RPV)
$\mathbf{a}_2 = 2\pi\frac{\mathbf{b}_3 \times \mathbf{b}_1}{V_0^*}$ (PV in terms of RPV)
$\mathbf{a}_3 = 2\pi\frac{\mathbf{b}_1 \times \mathbf{b}_2}{V_0^*}$ (PV in terms of RPV)
$V_0^* = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|$ (volume of reciprocal PUC)
$\quad = (2\pi)^3/V_0$ (in terms of V_0)

Verifying Definition of Reciprocal Primitive Vectors
Consider a Bravais lattice Λ spanned by primitive vectors $\{\mathbf{a}_i\}$
$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ (definition of reciprocal PVs $\{\mathbf{b}_j\}$)
$\mathbf{K} = m_1\mathbf{b}_1 + m_2\mathbf{R}_2 + m_3\mathbf{R}_3$ (reciprocal lattice vectors)
Goal: show the $\mathbf{b}_i$ are consistent with $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for all $\mathbf{R} \in \Lambda$
$\mathbf{K} \cdot \mathbf{R} = (m_i\mathbf{b}_i) \cdot (n_j\mathbf{a}_j)$ (summation notation)
$\quad = 2\pi(n_1m_1 + n_2m_2 + n_3m_3)$ (using $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$)
$\quad = 2\pi N$ (for some integer $N \in \mathbb{Z}$)
$\implies e^{i\mathbf{K}\cdot\mathbf{R}} = e^{2\pi i N} = 1$ (defs. of $\mathbf{b}$ and $\mathbf{K}$ are consistent)

First Brilloun Zone
Consider a Bravais lattice Λ spanned by primitive vectors $\{\mathbf{a}_i\}$
$\Lambda^* = \left\{ \mathbf{K} \mid e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda \right\}$ (the BL's RL)
The RL's Wigner-Seitz cell is called the *first Brillioun zone*.
The first BZ is defined analogously to the Wigner-Seitz cell in position space, i.e. the first BZ is the set of all $\mathbf{k}$ in reciprocal space closest to the origin $\mathbf{K} = \mathbf{0}$.
$\Omega_{\text{BZ1}} = \left\{ \mathbf{k} \in (\mathbb{R}^*)^3 : |\mathbf{k}| < |\mathbf{k} - \mathbf{K}| \text{ for all } \mathbf{K} \in \Lambda^* \right\}$

Reciprocal Lattices of Common BLs
Goal: compute and interpret the reciprocal primitive vectors for common Bravais lattices.

Simple Cubic Reciprocal Lattice
Consider a simple cubic lattice with lattice constant a
$\mathbf{a}_1 = a\,\hat{\mathbf{x}}$ (for review)
$\mathbf{a}_2 = a\,\hat{\mathbf{y}}$ (for review)
$\mathbf{a}_3 = a\,\hat{\mathbf{z}}$ (for review)
$\mathbf{b}_1 = \tfrac{2\pi}{a}\,\hat{\mathbf{x}}$
$\mathbf{b}_2 = \tfrac{2\pi}{a}\,\hat{\mathbf{y}}$

3

$\mathbf{b}_3 = \frac{2\pi}{a}\,\hat{\mathbf{z}}$

Interpretation: a SC lattice's reciprocal lattice is a SC lattice in reciprocal space with lattice constant $2\pi/a$.

FCC Reciprocal Lattice

Consider a FCC lattice with lattice constant a

$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$ (for review)
$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$ (for review)
$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$ (for review)
$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$
$\mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}})$
$\mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$

Interpretation: a FCC lattice's reciprocal lattice is a BCC lattice in reciprocal space with lattice constant $4\pi/a$.

BCC Reciprocal Lattice

Consider a BCC lattice with lattice constant a

$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$ (for review)
$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}})$ (for review)
$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$ (for review)
$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$
$\mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$
$\mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$

Interpretation: a BCC lattice's reciprocal lattice is a FCC lattice in reciprocal space with lattice constant $4\pi/a$.

Lattice Planes

Consider a Bravais lattice Λ spanned by primitive vectors $\{\mathbf{a}_i\}$
A *lattice plane* is a plane in position space passing through three non-colinear BL points $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$

Families of Lattice Planes

Defining a single lattice plane implicitly defines a family of lattice planes in which...

- all planes are parallel (have the same normal $\hat{\mathbf{n}}$)

- neighboring planes are separated by the same distance d

- the entire lattice plane family contains every lattice site in the Bravais lattice

Each family of lattice planes corresponds to a RL vector $\mathbf{K}$ normal to the lattice planes for which...
$\mathbf{K} = \frac{2\pi}{d}\,\hat{\mathbf{n}}$ (RL vector for a lattice plane family)
For two lattice sites $\mathbf{R}_i, \mathbf{R}_j$ in the i-th and j-th planes...
$|\mathbf{K} \cdot (\mathbf{R}_i - \mathbf{R}_j)| = 2\pi|i - j|$ (from geometrical arguments)
$\implies e^{i\mathbf{K}\cdot(\mathbf{R}_i - \mathbf{R}_j)} = 1$ for all $\mathbf{R}_i, \mathbf{R}_j \in \Lambda$
$\implies e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for all $\mathbf{R} \in \Lambda$ (BL closed under addition)
Conclusion: $\mathbf{K} = \frac{2\pi}{d}\,\hat{\mathbf{n}}$ satisfies the condition for a RL vector

Miller Indices

Purpose: Miller indices are used to define the RL vector $\mathbf{K} = \frac{2\pi}{d}\,\hat{\mathbf{n}}$ specifying a family of lattice planes.
Consider a Bravais lattice Λ spanned by the primitive vectors $\{\mathbf{a}_i\}$ and having reciprocal primitive vectors $\{\mathbf{b}_i\}$.
Define a lattice plane with the three non-colinear points $n_1\mathbf{a}_1$, $n_2\mathbf{a}_2$ and $n_3\mathbf{a}_3$ where $n_i \in \mathbb{Z}$ and let $\mathbf{K} = \frac{2\pi}{d}\,\hat{\mathbf{n}}$ be the reciprocal vector defining the lattice plane family.
$\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$ ($\mathbf{K}$ in terms of Miller indices)
Miller indices are conventionally written in lowest terms, i.e. with greatest common divisor equal to one.
The planes specified by the $(hk\ell)$ intersect integer multiples of the points $\mathbf{a}_1/h$, $\mathbf{a}_2/k$, and $\mathbf{a}_3/\ell$.
$(n_1\mathbf{a}_1) \cdot \mathbf{K} = (n_2\mathbf{a}_2) \cdot \mathbf{K} = (n_3\mathbf{a}_3) \cdot \mathbf{K} \equiv C$ (for lattice plane)
Apply $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ and $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$ to get...
$\implies n_1 h = n_2 k = n_3 \ell = C$
$\implies h : k : \ell = \frac{1}{n_1} : \frac{1}{n_2} : \frac{1}{n_3}$ (inverse ratio relationship)

X-Ray Scattering from Crystals

Motivation: x-ray scattering is used to experimentally determine crystal structure.
Restriction: we will consider only elastic scattering, for which pre- and post-scattering wavelengths are equal.
$\lambda = \lambda'$ (assuming elastic scattering)

Photon Energy for Constructive Interference

Goal: estimate photon energies at which scattered photons will interfere constructively in the crystal lattce
$a \sim 0.1\,\text{nm}$ (typical spacing between lattice points)
$\lambda \lesssim a$ (condition for interference on lattice)
$h\nu = \frac{hc}{\lambda} \gtrsim \frac{hc}{a} \sim \frac{1240\,\text{eV nm}}{0.1\,\text{nm}}$ (for photon with $\lambda \lesssim a$)
    $= 12.4\,\text{keV}$ (min. photon energy for interference)
Conclusion: constructive interference from a crystal lattice is possible for photons with keV energy or larger (i.e. x-rays).

Bragg Formulation of Scattering

Model: in the Bragg formulation, x-rays scatter from lattice planes and not from discrete lattice sites.
Let $\mathbf{k}$ denote incident wave vector
Let $\mathbf{k}'$ denote scattered wave vector
Let θ denote glancing angle between $\mathbf{k}$ and lattice plane
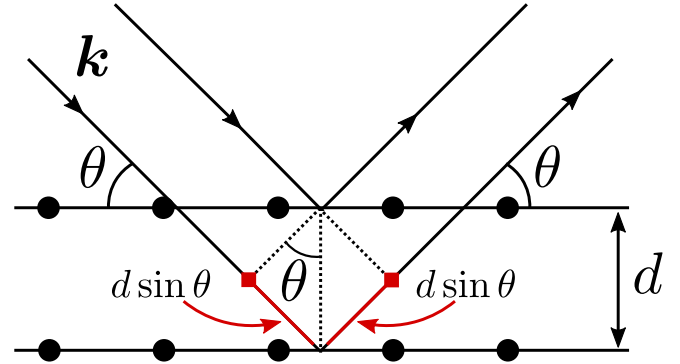
Figure 1: The geometry of Bragg scattering.

Bragg Interference Condition

Consider x-rays incident at glancing angle θ on a family of lattice planes with spacing d.
$|\mathbf{k}| = |\mathbf{k}'| \equiv k$ (assuming elastic scattering)
The difference in path length Δx for x-rays scattering from neighboring lattice planes is...
$\Delta x = 2d\sin\theta$ (for neighboring planes)
$\Delta\phi = k\Delta x$ (phase difference btwn. scattered x-rays)
$\Delta\phi = k\Delta x = 2\pi n$ (constructive interference condition)
$\frac{2\pi}{\lambda} \cdot (2d\sin\theta) = 2\pi n$ (in terms of wavelength λ)
$2d\sin\theta = n\lambda$ (**Bragg interference condition**)

Von Laue Formulation of Scattering

Model: in the von Laue formulation, x-rays scatter from discrete lattice sites rather than from entire lattice planes.
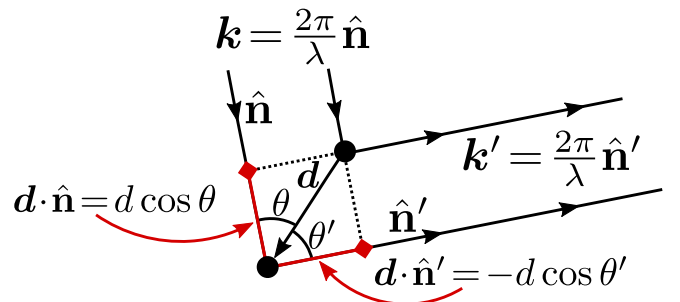
Figure 2: The geometry of von Laue scattering.

Von Laue Interference Condition

Let $\mathbf{k} \equiv \frac{2\pi}{\lambda}\,\hat{\mathbf{n}}$ denote incident wave vector

Let $\mathbf{k}' \equiv \frac{2\pi}{\lambda}\,\hat{\mathbf{n}}'$ denote scattered wave vector

$|\mathbf{k}| = |\mathbf{k}'| \implies \lambda = \lambda'$ (assuming elastic scattering)

Consider two lattice sites connected by the vector $\mathbf{d}$

Let θ denote angle between $\mathbf{d}$ and $\hat{\mathbf{n}}$

Let θ' denote angle between $\mathbf{d}$ and $\hat{\mathbf{n}}'$

The difference in path length Δx for x-rays scattering from neighboring lattice sites is...

$\Delta x = d\cos\theta + d\cos\theta' = \mathbf{d}\cdot(\hat{\mathbf{n}} - \hat{\mathbf{n}}')$ (for neighboring sites)

$\Delta\phi = k\Delta x$ (phase difference btwn. scattered x-rays)

$\Delta\phi = k\Delta x = 2\pi m$ (constructive interference condition)

$\frac{2\pi}{\lambda}\mathbf{d}\cdot(\hat{\mathbf{n}} - \hat{\mathbf{n}}') = 2\pi m$ (in terms of wavelength λ)

$\mathbf{d}\cdot(\mathbf{k} - \mathbf{k}') = 2\pi m$ (in terms of wave vector $\mathbf{k}$)

Concept: constructive interference occurs when above condition holds for *all* $\mathbf{d}$ in the BL. Let $\mathbf{d} \to \mathbf{R}$ to get...

$\mathbf{R}\cdot(\mathbf{k} - \mathbf{k}') = 2\pi m$ (**von Laue interference condition**)

Alternate Formulation of the von Laue Condition

Consider a Bravais lattice Λ with reciprocal lattice Λ^*

$\mathbf{R}\cdot(\mathbf{k} - \mathbf{k}') = 2\pi m \,\forall\, \mathbf{R} \in \Lambda$ (vL interference condition)

$e^{i\mathbf{R}\cdot(\mathbf{k}-\mathbf{k}')} = e^{2\pi i m} = 1$ (exponentiating)

Compare $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = 1$ to definition $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ of a general reciprocal lattice vector $\mathbf{K}$ to conclude...

The von Laue interference condition is met if the incident and scattered wave vectors obey $\mathbf{k} - \mathbf{k}' = \mathbf{K}$ *for some* $\mathbf{K} \in \Lambda^*$!

$\mathbf{k} - \mathbf{k}' = \mathbf{K}$ (**von Laue interference condition**)

$(\mathbf{k}')^2 = (\mathbf{k} - \mathbf{K})^2$ (rearranged and squared)

$k^2 = k^2 - 2\mathbf{k}\cdot\mathbf{K} + K^2$ ($k = k'$ for elastic scattering)

Let $\hat{\mathbf{K}} = \mathbf{K}/|\mathbf{K}|$ and simplify to get...

$\mathbf{k}\cdot\hat{\mathbf{K}} = \frac{K}{2}$ (alternate interference condition)

Bragg Plane

From above, an incident WV $\mathbf{k}$ scatters constructively if...

$\mathbf{k}\cdot\hat{\mathbf{K}} = \frac{K}{2}$ for some $\mathbf{K} \in \Lambda^*$ (interference condition)

This condition defines a plane in reciprocal space called a *Bragg plane*, which perpendicularly bisects the $\mathbf{K}$ from the interference condition $\mathbf{k} - \mathbf{k}' = \mathbf{K}$ or $\mathbf{k}\cdot\hat{\mathbf{K}} = K/2$.
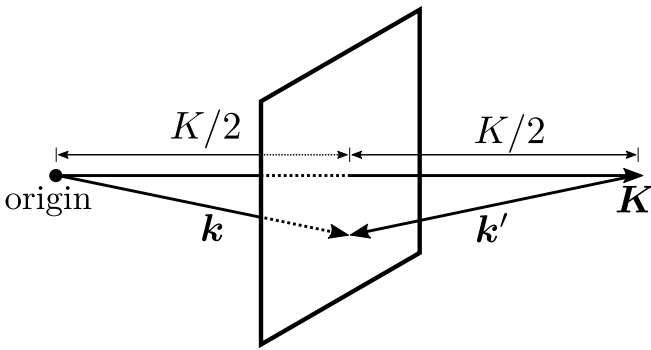
Figure 3: A Bragg plane defined by $\mathbf{K}$.

Equivalence of the Bragg and Von Laue Conditions

Goal: show Bragg and von Laue conditions for constructive interference are equivalent

Consider a family of lattice planes with spacing d defined by the reciprocal lattice vector $\mathbf{K} = \frac{2\pi n}{d}\,\hat{\mathbf{n}}$ where $n \in \mathbb{N}$.

Let $\mathbf{k}$ denote incident wave vector

Let $\mathbf{k}'$ denote scattered wave vector

Let θ denote glancing angle between $\mathbf{k}$ and lattice plane

$\mathbf{k} - \mathbf{k}' = \mathbf{K}$ (von Laue condition)

The von Laue condition requires a relationship between $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{K}$ as shown in the figure below...
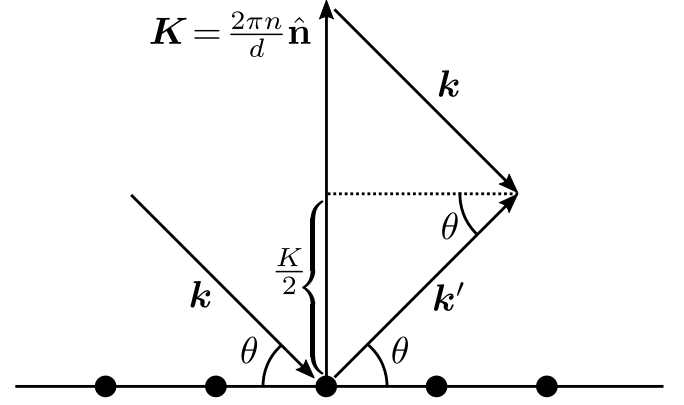
Figure 4: Geometry for showing the equivalence of the Bragg and von Laue interference conditions.

$\theta = \theta'$ (law of reflection)

$\implies k'\sin\theta = K/2$ (see figure)

$K/2 = k\sin\theta$ ($k = k'$ for elastic scattering)

$\frac{\pi n}{d} = \frac{2\pi}{\lambda}\sin\theta$ (using $K = 2\pi n/d$ and $k = 2\pi/\lambda$)

$\implies 2d\sin\theta = n\lambda$ (Bragg condition)

Ewald Sphere Formulation of Scattering

Summary: a geometric method for determining which incident wave vectors $\mathbf{k}$ will scatter constructively from a crystal lattice. The Ewald sphere for a given incident $\mathbf{k}$ is defined in reciprocal space as follows:

- Define an origin centred on a reciprocal lattice site

- The origin lies on the sphere's surface

- The incident $\mathbf{k}$ points from the origin to sphere's center

- The Ewald sphere has radius $|\mathbf{k}| = 2\pi/\lambda$

If the thus-defined sphere's surface intersects other RL vectors, the incident $\mathbf{k}$ will scatter with constructive interference.

Structure Factors

Motivation: analyze x-ray scattering from crystals with multiple atomic scatterers of the same element per primitive unit cell.

Let $\mathbf{R}_i$ denote positions of Bravais lattice sites

Positions of atoms in a PUC are given by the basis $\{\mathbf{d}_j\}$

$\mathbf{R}_{\mathrm{at}}^{ij} = \mathbf{R}_i + \mathbf{d}_j$ (position of j-th atom at i-th lattice site)

$\mathbf{K}\cdot\mathbf{R}_{\mathrm{at}}^{ij} = 2\pi n + \mathbf{K}\cdot\mathbf{d}_j$ (since $\mathbf{K}\cdot\mathbf{R} = 2\pi n$)

Conclusion: different RL vectors will lead to different scattering intensities from a given atom because of the $\mathbf{K}\cdot\mathbf{d}_j$ term

Geometric Structure Factor

$\mathbf{K}\cdot\mathbf{R}_{\mathrm{at}}^{ij} = 2\pi n + \mathbf{K}\cdot\mathbf{d}_j$ (since $\mathbf{K}\cdot\mathbf{R} = 2\pi n$)

$\mathbf{K}\cdot\mathbf{R}_{\mathrm{at}}^{ik} = 2\pi n + \mathbf{K}\cdot\mathbf{d}_k$ (since $\mathbf{K}\cdot\mathbf{R} = 2\pi n$)

$\Delta\phi = \mathbf{K}\cdot(\mathbf{d}_j - \mathbf{d}_k)$ (phase difference btwn. rays scattered from different atoms in the same lattice site)

$e^{i\Delta\phi} = e^{i\mathbf{K}\cdot(\mathbf{d}_j - \mathbf{d}_k)}$ (ratio of amplitudes of rays scattered from j-th and k-th atoms)

$S_{\mathbf{K}} \equiv \sum_j e^{i\mathbf{K}\cdot\mathbf{d}_j}$ (**geometric structure factor**)

Interpretation: the GSF expresses the extent to which x-rays scattered from the atoms in a given PUC diminish the intensity of the interference peak associated with a given $\mathbf{K}$ via the von Laue interference condition $\mathbf{k} - \mathbf{k}' = \mathbf{K}$.

Generalization: Atomic Structure Factor

Motivation: analyze x-ray scattering from crystals with atoms of *different* elements in each primitive unit cell.

Concept: different elements produce different scattering intensities due to differences in electron cloud structure.

Let $\mathbf{R}_i$ denote positions of Bravais lattice sites

Positions of atoms in a PUC are given by the basis $\{\mathbf{d}_j\}$

Let ρ_j denote j-th atom's electron cloud charge density

Let Z_j denote j-th atom's atomic number

$S_{\mathbf{K}}^{\text{at}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$ (**atomic structure factor**)

f_j is the dimensionless scattering amplitude of the j-th atom

$$
\begin{aligned}
f_j(\mathbf{K}) &= -\frac{1}{e_0} \iiint e^{i\mathbf{K}\cdot\mathbf{r}} \rho(\mathbf{r})\,\mathrm{d}V && \text{(scattering amplitude)}\\
&\approx -\frac{1}{e_0} \iiint_{\text{cloud}} e^{i\mathbf{K}\cdot\mathbf{r}} \rho(\mathbf{r})\,\mathrm{d}V && (\rho \sim 0 \text{ outside } e^- \text{ cloud})\\
&\approx -\frac{1}{e_0} \iiint_{\text{cloud}} \rho(\mathbf{r})\,\mathrm{d}V && \text{(for } \mathbf{K}\cdot\mathbf{r} \ll 1 \text{ in } e^- \text{ cloud})\\
&\sim Z_j && \left(\text{using } \iiint_{\text{cloud}} \rho\,\mathrm{d}V \sim -Ze_0\right)
\end{aligned}
$$

Free Electrons

Sommerfeld Free Electron Theory

Goal: describe the behavior of *free* electrons in crystals using the *single*-particle stationary Schrödinger equation:

$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r})$ (stationary Schrödinger eq.)

$\psi_{\mathbf{k}} = Ae^{i\mathbf{k}\cdot\mathbf{r}}$ (ansatz for electron eigenfunctions)

$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$ (corresponding energy eigenvalues)

$= \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$ (by components)

Model for Crystal
Model crystal as cuboid with...

- side lengths L_x, L_y, L_z,

- lattice constants a_x, a_y, a_z,

- number of lattice sites N_x, N_y, N_z,

- primitive vectors $\mathbf{a}_x$, $\mathbf{a}_y$, $\mathbf{a}_z$, and

- reciprocal primitive vectors $\mathbf{b}_x$, $\mathbf{b}_y$, $\mathbf{b}_z$...

...in the $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ Cartesian directions, respectively.

$V = L_x L_y L_z$ (crystal volume)

$\implies \psi_{\mathbf{k}}(\mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}} \to \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}$ ($A = \frac{1}{\sqrt{V}}$ for normalization)

Periodic Boundary Conditions
Concept: e^- is confined to crystal interior (and not all space). Boundary conditions on the electron wave function ψ must reflect this confinement.

Important: for macroscopic crystals with $L \gg a$, bulk properties are unaffected by choice of boundary conditions.

$\implies$ We choose *periodic* BC for analytical convenience.

$\psi_{\mathbf{k}}(x, y, z) \equiv \psi_{\mathbf{k}}(x + L_x, y + L_y, z + L_z)$ (**PBC**)

$\implies k_x = \frac{2\pi}{L_x}n_x, \ n_x \in \mathbb{Z}$ (result of PBC)

$\implies k_y = \frac{2\pi}{L_y}n_y, \ n_y \in \mathbb{Z}$ (result of PBC)

$\implies k_z = \frac{2\pi}{L_z}n_z, \ n_z \in \mathbb{Z}$ (result of PBC)

Alternatively, in terms of N_i and a_i, values of k_i read...

$k_x = \frac{2\pi}{N_x a_x}n_x$ (using $L_x = N_x a_x$)

$k_y = \frac{2\pi}{N_y a_y}n_y$ (using $L_y = N_y a_y$)

$k_z = \frac{2\pi}{N_z a_z}n_z$ (using $L_z = N_z a_z$)

Conclusion: PBC quantize the wave vector $\mathbf{k}$!

Quantization of k Space
Goal: determine how many allowed values of $\mathbf{k}$ are contained per unit volume of $\mathbf{k}$ space in crystal of volume V.

Assume $L_x = L_y = L_z \equiv L$ (for notational simplicity)

Review: the k axes are quantized in units of $2\pi/L$.

$\Delta\mathbf{k} = \frac{(2\pi)^3}{L^3} = \frac{8\pi^3}{V}$ (spacing btwn. allowed values of $\mathbf{k}$)

Consider a region of $\mathbf{k}$ space with volume $\Omega \gg \Delta\mathbf{k}$.

Concept: the number $N_{\mathbf{k}}$ of allowed $\mathbf{k}$ in Ω equals the volume of Ω divided by the volume $\Delta\mathbf{k}$ around a single $\mathbf{k}$ point.

$N_{\mathbf{k}} = \frac{\Omega}{\Delta\mathbf{k}} = \frac{\Omega V}{8\pi^3}$ (number of discrete $\mathbf{k}$ in Ω)

$n_{\mathbf{k}} = \frac{N_{\mathbf{k}}}{\Omega} = \frac{V}{8\pi^3}$ (density of discrete $\mathbf{k}$ in Ω)

$n_{\mathbf{k}} = \frac{V}{8\pi^3}$ (**k-space density of k values**)

Interpreting k as Free Electron Momentum
$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}$ (review: electron wave function)

$\hat{\mathbf{p}} = -i\hbar\nabla$ (quantum-mechanical momentum operator)

$\hat{\mathbf{p}}\psi_{\mathbf{k}} = +\frac{\hbar\mathbf{k}}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}\psi_{\mathbf{k}}$ (action of $\hat{\mathbf{p}}$ on $\psi_{\mathbf{k}}$)

Conclusion: free electron eigenfunctions $\psi_{\mathbf{k}}$ are eigenfunctions of the momentum operator with eigenvalues $\hbar\mathbf{k}$

$\implies \hbar\mathbf{k}$ may be interpreted as momentum of a free electron

Heuristic comment: free electron momentum is exactly known, so (by uncertainty principle) position is completely uncertain.

$\implies$ Free electrons are completely delocalized in the crystal containing them.

Fermi Sphere
Consider the $T = 0\,\mathrm{K}$ ground state of N free electrons.

Goal: build up the N-electron ground state in accordance with the Pauli exclusion principle.

$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$ (review: free e^- energy eigenvalues)

$\implies e^-$ occupying levels with larger k have larger energy

Idea: beyond some large enough k (or large enough $E_{\mathbf{k}}$) electron levels in a ground state crystal will no longer be occupied.

The *Fermi wave vector* k_{F} is the value of k separating occupied and unoccupied *free* electron levels at $T = 0\,\mathrm{K}$.

The *Fermi sphere* is the sphere in $\mathbf{k}$ space of radius k_{F}, and separates occupied and unoccupied *free* e^- levels at $T = 0\,\mathrm{K}$.

The Fermi sphere's radius k_{F} defines the following...

$V_{\mathrm{F}}^* \equiv \frac{4\pi}{3}k_{\mathrm{F}}^3$ (volume of Fermi sphere)

$E_{\mathrm{F}} \equiv \frac{\hbar^2 k_{\mathrm{F}}^2}{2m}$ (Fermi energy)

$T_{\mathrm{F}} \equiv \frac{E_{\mathrm{F}}}{k_{\mathrm{B}}}$ (Fermi temperature)

$v_{\mathrm{F}} \equiv \frac{\hbar k_{\mathrm{F}}}{m}$ (Fermi velocity)

Number of Occupied Electron Levels I
Goal: determine number N_{e} and volume density n_{e} of occupied free electron levels in an N-electron gas's ground state.

$V_{\mathrm{F}}^* = \frac{4\pi}{3}k_{\mathrm{F}}^3$ (volume of Fermi sphere)

$\Delta\mathbf{k} = \frac{(2\pi)^3}{L^3} = \frac{(2\pi)^3}{V}$ (spacing btwn. discrete $\mathbf{k}$ states)

To determine N_{e}, consider the following...

- The $\mathbf{k}$-space volume of one allowed $\mathbf{k}$ is $\Delta\mathbf{k} = \frac{(2\pi)^3}{V}$

- All occupied ground state $\mathbf{k}$ reside in a volume V_{F}^*

- Each allowed $\mathbf{k}$ permits two electron levels, one for e^- with spin up and one for e_- with spin down.

$\implies$ number of occupied free e^- levels in the ground state will equal total $\mathbf{k}$-space volume V_{F}^*, divided by $\Delta\mathbf{k}$, times 2.

$N_{\mathrm{e}} = 2 \cdot \frac{V_{\mathrm{F}}^*}{\Delta\mathbf{k}}$ (factor of 2 from e^- spin)

$= \frac{k_{\mathrm{F}}^3}{3\pi^2}V$ (number of occupied free e^- levels)

$k_{\mathrm{F}}^3 = 3\pi^2\frac{N_{\mathrm{e}}}{V}$ (useful rearrangement)

$n_{\mathrm{e}} = \frac{N_{\mathrm{e}}}{V} = \frac{k_{\mathrm{F}}^3}{3\pi^2}$ (volume density of free e^- levels)

Density of Levels
Goal: determine density per unit energy of occupied free electron levels in an N-electron gas's ground state.

$E_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m}$ (review: Fermi energy)

$N_{\mathrm{e}} = \frac{k_{\mathrm{F}}^3}{3\pi^2}$ (review: number of e^- levels)

$= \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E_{\mathrm{F}}^{3/2}$ (in terms of E_{F})

$\to \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{3/2}$ (generalizing $E_{\mathrm{F}} \to E$)

$\mathcal{D}(E) \equiv \frac{\mathrm{d}N_{\mathrm{e}}}{\mathrm{d}E} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$ (**density of levels**)

Interpretation: Density of levels $\mathcal{D}$ (units energy^{-1}) expresses the number of available electron energy levels per unit energy in a free electron gas at energy E.

Review: Fermi-Dirac Distribution
Consider a system of non-interacting fermions with chemical potential μ in thermodynamic equilibrium at temperature T.

Chemical potential μ is the (temperature-dependent) energy needed to add one additional fermion to the system; in general the added fermion must have energy larger than all present fermions to satisfy the Pauli exclusion principle.

$\beta \equiv \frac{1}{k_{\mathrm{B}}T}$ (thermodynamic beta)

$f(E) = \frac{1}{e^{\beta(E-\mu)}+1}$ (**Fermi-Dirac distribution**)

$f(E) \in [0,1]$ for $E > 0$ (by construction)

The FD distribution expresses the probability that a fermion level with energy E is occupied in the given fermion system at temperature T.

Chemical Potential and Fermi Energy

$$\lim_{T \to 0\,\mathrm{K}} f(E) = \begin{cases} 1 & E < \mu \\ 0 & E > \mu \end{cases} \quad \text{(limit as } T \to 0\,\mathrm{K)}$$

Simultaneously: E_F is the highest-occupied energy in a ground state (i.e. at $T = 0\,\mathrm{K}$).

Conclusion: for $f(E)$ to be consistent with earlier analysis of free electron gas ground state...

$E_\mathrm{F} = \lim_{T \to 0\,\mathrm{K}} \mu(T)$ (in a free electron gas)

Number of Occupied Electron Levels II

Consider a system of free electrons with known density of levels $\mathcal{D}$ and Fermi-Dirac distribution $f(E)$

Goal: express the number N_e of occupied e^- levels in a free-electron gas in terms of $\mathcal{D}(E)$ and $f(E)$.

$N_\mathrm{e} = \int_0^\infty f(E)\mathcal{D}(E)\,\mathrm{d}E$ (number of occupied e^- states)

Interpretation: $\mathcal{D}(E)$ gives density of *available* states and $f(E)$ gives probability a state is *occupied*; the product $f(E)\mathcal{D}(E)$ integrated over E gives the total number of occupied states.

$N_\mathrm{e} = \int_0^{E_\mathrm{F}} \mathcal{D}(E)\,\mathrm{d}E$ (at $T = 0\,\mathrm{K}$)

Volume-Normalized Density of Levels

$\mathcal{D}(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$ (review: density of levels)

$g(E) \equiv \frac{\mathcal{D}}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$ (volume-normalized DoL)

Interpretation: volume-normalized density of levels (units energy^{-1} volume^{-1}) expresses the number of available electron energy levels per unit energy per unit volume in a free electron gas at energy E.

Two notes:

- g and $\mathcal{D}$ are commonly called "density of state". (Density of levels is used here to distinguish between single-electron levels and the state of an entire e^- gas.)

- $g(E)$ is used far more commonly than $\mathcal{D}(E)$, so $g(E)$ is usually called just the density of states/levels, omitting "volume-normalized".

Alternate Expressions for Densities of Levels

$E_\mathrm{F} = \frac{\hbar^2 k_\mathrm{F}^2}{2m}$ (review: Fermi energy)

$k_\mathrm{F}^3 = 3\pi^2 \frac{N_\mathrm{e}}{V}$ (review: relating k_F and N_e)

$\left(\frac{2m}{\hbar^2}\right)^{3/2} = \frac{N_\mathrm{e}}{V}\frac{3\pi^2}{E_\mathrm{F}^{3/2}}$ (combined and rearranged)

Let $n_\mathrm{e} \equiv \frac{N_\mathrm{e}}{V}$ (volume density of occupied e^- levels)

$\mathcal{D}(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$ (original expression)

$= \frac{3}{2}\frac{N_\mathrm{e}}{E_\mathrm{F}}\sqrt{\frac{E}{E_\mathrm{F}}}$ (using above identity)

$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$ (original expression)

$= \frac{3}{2}\frac{n_\mathrm{e}}{E_\mathrm{F}}\sqrt{\frac{E}{E_\mathrm{F}}}$ (using $g = \frac{\mathcal{D}}{V}$ and $n_\mathrm{e} = \frac{N_\mathrm{e}}{V}$)

Technique: Approximating Sums over k with Integrals

Goal: simplify sums over $\mathbf{k}$ of the form $\frac{1}{V}\sum_{\mathbf{k}} F(\mathbf{k})$, where $\mathbf{k}$ takes all values allowed by the crystal's periodic BC.

$\Delta\mathbf{k} = \frac{(2\pi)^3}{L^3} = \frac{8\pi^3}{V}$ (review: spacing between allowed $\mathbf{k}$)

$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{1}{\Delta\mathbf{k}}\sum_{\mathbf{k}} F(\mathbf{k})\Delta\mathbf{k}$ (multiplying/dividing by $\mathbf{k}$)

$= \frac{V}{8\pi^3}\sum_{\mathbf{k}} F(\mathbf{k})\Delta\mathbf{k}$ (from definition of $\mathbf{k}$)

$\frac{1}{V}\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{1}{8\pi^3}\sum_{\mathbf{k}} F(\mathbf{k})\Delta\mathbf{k}$ (rearranged)

Take macroscopic limit as $V \to \infty$ and $\Delta\mathbf{k} \to 0$ to get...

$\frac{1}{V}\sum_{\mathbf{k}} F(\mathbf{k}) \to \iiint F(\mathbf{k})\frac{\mathrm{d}\mathbf{k}}{8\pi^3}$ (result: $\sum_{\mathbf{k}} \to \iiint \mathrm{d}^3\mathbf{k}$)

Technique: Simplifying Integrals with $g(E)$

For integrals over $\mathrm{d}^3\mathbf{k}$ with integrands depending only on $k = |\mathbf{k}|$, we can make the substitution...

$\frac{\mathrm{d}^3\mathbf{k}}{4\pi^3} = g(E)\,\mathrm{d}E$ (result: simplifying $\iiint \mathrm{d}^3\mathbf{k}$)

$\iiint F(E(\mathbf{k}))\frac{\mathrm{d}^3\mathbf{k}}{4\pi^3} = \int F(E)g(E)\,\mathrm{d}E$ (example usage)

<u>Derivation</u>

$E = \frac{\hbar^2 k^2}{2m}$ (free electron energy)

$\implies \sqrt{E} = \frac{\hbar k}{\sqrt{2m}}$ and $\mathrm{d}E = \frac{\hbar^2 k}{m}\,\mathrm{d}k$

Assuming the integrand depends only on $|\mathbf{k}| = k$...

$\frac{\mathrm{d}^3\mathbf{k}}{4\pi^3} = \frac{(4\pi k^2\,\mathrm{d}k)}{4\pi^3} = \frac{k^2}{\pi^2}\,\mathrm{d}k$ (converting to spherical coordinates)

$g(E)\,\mathrm{d}E = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}\cdot\frac{\hbar^2 k}{m}\,\mathrm{d}k$

$= \frac{k^2}{\pi^2}\,\mathrm{d}k$ (after simplifying)

$= \frac{\mathrm{d}^3\mathbf{k}}{4\pi^3}$ (converting from spherical coordinates)

Average Internal Energy

The average internal energy per unit volume of free electron gas with known FD distribution $f(E)$ is

$\langle u \rangle = \frac{2}{V}\sum_{\mathbf{k}} f(E(k))E(k)$ (**free e^- internal energy**)

Interpretation: factor of 2 from e^- spin; sum runs over the discrete k required by PBC; FD distribution $f(E)$ serves as weight for e^- energy $E(k)$ at a given k.

Idea: assuming k are closely spaced, approximate the sum with an integral to get...

$\langle u \rangle \approx \frac{2}{V}\cdot\left[\frac{1}{V_0^*}\iiint f(E)E(k)\,\mathrm{d}^3\mathbf{k}\right]$

$V_0^* = \frac{(2\pi)^3}{V}$ is spacing btwn. discrete values of $\mathbf{k}$

$\langle u \rangle = \frac{1}{4\pi^3}\iiint f(E)E(k)\,\mathrm{d}^3\mathbf{k}$ (using $V_0^* = (2\pi)^3/V$)

$= \int_0^\infty f(E)g(E)E\,\mathrm{d}E$ (using $\frac{\mathrm{d}^3\mathbf{k}}{4\pi^3} = g(E)\,\mathrm{d}E$)

$\langle u \rangle \approx \int_0^\infty f(E)g(E)E\,\mathrm{d}E$ (**free e^- internal energy**)

Internal Energy at Zero Kelvin

$\langle u \rangle \approx \int_0^\infty f(E)g(E)E\,\mathrm{d}E$ (in general)

$$\lim_{T \to 0\,\mathrm{K}} f(E) = \begin{cases} 1 & E < E_\mathrm{F} \\ 0 & E > E_\mathrm{F} \end{cases} \quad \text{(review: low-temp. limit)}$$

$g(E) = \frac{3}{2}\frac{n_\mathrm{e}}{E_\mathrm{F}}\sqrt{\frac{E}{E_\mathrm{F}}}$ (review: expression for $g(E)$)

$g(E_\mathrm{F}) = \frac{3}{2}\frac{n_\mathrm{e}}{E_\mathrm{F}}$ (at $E = E_\mathrm{F}$)

$\lim_{T \to 0\,\mathrm{K}}\langle u \rangle = \int_0^{E_\mathrm{F}} Eg(E)\,\mathrm{d}E$

$= \int_0^{E_\mathrm{F}} E\cdot\frac{3}{2}\frac{n_\mathrm{e}}{E_\mathrm{F}}\sqrt{\frac{E}{E_\mathrm{F}}}\,\mathrm{d}E$ (substituting in $g(E)$)

$= \frac{3}{5}n_\mathrm{e}E_\mathrm{F}$ (internal energy at zero kelvin)

Sommerfeld Expansion

Consider a function of energy $H(E)$ describing a system with Fermi-Dirac distribution $f(E)$, Fermi temperature T_F, and chemical potential μ. Without derivation, the *Sommerfeld expansion* of $H(E)$ is for small temperatures $T < T_\mathrm{F}$ is...

$$\int_{-\infty}^\infty f(E)H(E)\,\mathrm{d}E = \int_{-\infty}^\mu H(E)\,\mathrm{d}E + \frac{\pi^2}{6}(k_\mathrm{B}T)^2\frac{\mathrm{d}H}{\mathrm{d}E}\Big|_{E=\mu} + \mathcal{O}(k_\mathrm{B}T)^4$$

Conservation of Electron Number

Important concept: the total number of electrons in a crystal is constant $\implies N_\mathrm{e} \neq N_\mathrm{e}(T)$

$N_\mathrm{e}(T)\big|_{T=0} = N_\mathrm{e}(T)\big|_{T>0}$

$n_\mathrm{e}(T)\big|_{T=0} = n_\mathrm{e}(T)\big|_{T>0}$

$n_\mathrm{e} = \int_0^\infty f(E)g(E)\,\mathrm{d}E$ (in general)

$n_\mathrm{e} = \int_0^{E_\mathrm{F}} g(E)\,\mathrm{d}E$ (at $T = 0\,\mathrm{K}$)

By conservation of electron number, it follows that...

$\implies \int_0^\infty f(E)g(E)\,\mathrm{d}E = \int_0^{E_\mathrm{F}} g(E)\,\mathrm{d}E$ (since $n_\mathrm{e} \neq n_\mathrm{e}(T)$)

Sommerfeld Expansion of Electron Number Density

$n_e = \int_0^\infty f(E)g(E)\,dE$ $\qquad$ (in general)

Plan: use Sommerfeld expansion with $H(E) = g(E)$ and get...

$$n_e \approx \int_0^\mu g(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu)$$
$$= \int_0^{E_F} g(E)\,dE + \int_{E_F}^\mu g(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu)$$
$$= n_e + \int_{E_F}^\mu g(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) \quad \text{(1st integral is } n_e)$$
$$\implies \int_{E_F}^\mu g(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) = 0 \quad \text{(cancelling } n_e)$$

Sommerfeld Expansion of Chemical Potential

Goal: approximately compute $\mu(T)$ for low temperatures

$\mu(T) = E_F \pm \text{corrections}$ $\qquad$ (ansatz)

$\int_{E_F}^\mu g(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) = 0$ $\quad$ (from expansion of n_e)

To proceed, we make the following approximations...

(i) $\int_{E_F}^\mu g(E)\,dE \approx (\mu - E_F)g(E_F)$

(ii) $g'(\mu) \approx g'(E_F)$

$\implies (\mu - E_F)g(E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F) = 0$

$\mu(T) = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_F)}{g(E_F)}$ $\qquad$ (rearranged)

$g(E) \sim \sqrt{E} = E^{1/2}$ $\qquad$ (in general; for review)

$\implies g'(E) \sim \frac{1}{2}E^{-1/2}$ and $\frac{g'(E_F)}{g(E_F)} = \frac{1}{2E_F}$

Substitute $\frac{g'(E_F)}{g(E_F)} = \frac{1}{2E_F}$ into the $\mu(T)$ to get...

$\mu(T) = E_F - \frac{\pi^2}{12 E_F}(k_B T)^2$ $\qquad$ (**Sommerfeld expansion of** μ)

$\mu(T) = E_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2\right]$ $\qquad$ (rearranged)

$= E_F\left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right]$ $\qquad$ (in terms of T_F)

Sommerfeld Expansion of Internal Energy

$\langle u \rangle = \int_0^\infty f(E)g(E)E\,dE$ $\qquad$ (in general)

For shorthand, let $\langle u \rangle \to u$

Plan: use Sommerfeld expansion with $H(E) = g(E)E$ to get... (new notation)

$$u(T) \approx \int_0^\mu g(E)E\,dE + \frac{\pi^2}{6}(k_B T)^2 \frac{d}{dE}\big[Eg(E)\big]_{E=\mu}$$
$$= \int_0^\mu g(E)E\,dE + \frac{\pi^2}{6}(k_B T)^2\big[g(\mu) + \mu g'(\mu)\big]$$
$$= \int_0^{E_F} g(E)E\,dE + \int_{E_F}^\mu g(E)E\,dE \quad \text{(splitting integral)}$$
$$+ \frac{\pi^2}{6}(k_B T)^2\big[g(\mu) + \mu g'(\mu)\big]$$

To proceed, we make the following approximations...

(i) $\int_{E_F}^\mu g(E)E\,dE \approx (\mu - E_F)g(E_F)E_F$

(ii) $g(\mu) \approx g(E_F)$

(iii) $\mu g'(\mu) \approx E_F g'(E_F)$

$\implies u(T) \approx \int_0^{E_F} g(E)E\,dE + (\mu - E_F)E_F g(E_F)$
$+ \frac{\pi^2}{6}(k_B T)^2\big[g(E_F) + E_F g'(E_F)\big]$

$u_0 \equiv u(T)\big|_{T \to 0\,K} = \int_0^{E_F} g(E)E\,dE$ $\quad$ (for review; low T limit)

$\implies u(T) \approx u_0 + (\mu - E_F)E_F g(E_F)$ $\qquad$ (recognizing u_0)
$+ \frac{\pi^2}{6}(k_B T)^2\big[g(E_F) + E_F g'(E_F)\big]$

From the Sommerfeld of Chemical Potential recall...

$(\mu - E_F)g(E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F) \approx 0$

$\implies u(T) \approx u_0 + \frac{\pi^2}{6}(k_B T)^2 g(E_F)$ $\quad$ (**Sommerfeld exp. of** u)

Sommerfeld Expansion of Heat Capacity

$c_V \equiv \left(\frac{\partial u}{\partial T}\right)_{V, N_e}$ $\quad$ (specific heat capacity at constant volume)

$u \approx u_0 + \frac{\pi^2}{6}(k_B T)^2 g(E_F)$ $\qquad$ (Sommerfeld exp. of u)

$\implies c_V = \frac{\partial u}{\partial T} = \frac{\pi^2}{3}g(E_F)k_B^2 T$

$g(E_F) = \frac{3}{2}\frac{n_e}{E_F}$ $\qquad$ (review: $g(E)$ at $E = E_F$)

$\implies c_V = \frac{\pi^2}{2}\frac{n_e}{E_F}k_B^2 T$ $\qquad$ (**Sommerfeld expansion of** c_V)

$= \frac{\pi^2}{2}n_e k_B \frac{T}{T_F}$ $\qquad$ (in terms of T_F)

Lesson: the specific heat capacity of a free electron gas is proportional to temperature as $c_V \propto T$

In Passing: Molar Heat Capacity

$C \equiv \frac{z N_A k}{n_e}c_V$ $\qquad$ (molar heat capacity)

z is material's valance (number of e^- contributed to conduction)

N_A is Avogadro's constant

$C = \frac{\pi^2}{2}z N_A k_B \frac{T}{T_F}$ $\qquad$ (substituting in c_V)

$= \frac{\pi^2}{2}z R \frac{T}{T_F}$ $\qquad$ (using gas constant $R \equiv k_B N_A$)

$\equiv \gamma T$ $\qquad$ (defining $\gamma \equiv \frac{\pi^2 R Z}{2}$)

Drude Model of Conduction

The Drude model models the conduction electrons in a metal as an ideal classical monoatomic gas.

Assumptions:

- Conduction electrons may collide with ion cores, which are rigidly fixed, but both electron-electron and electron-ion interactions are otherwise negligible. Electrons move according to Newton's law between collisions.

- Collisions are random and instantaneous.

- Collision probability per unit time is given by the mean free time parameter τ. The probability dP that a randomly-chosen electron collide with an ion in the interval dt is $dP = dt/\tau$.

- Electrons can achieve thermal equilibrium with their surroundings via collisions only and the speed of an e^- emerging from a collision depends only on the temperature at the point of collision.

Current Density in the Drude Model

Consider a single electron in a metal exposed to a homogeneous external electric field $\boldsymbol{\mathcal{E}}(t) = \boldsymbol{\mathcal{E}}_0 e^{-i\omega t}$.

Model collisions with velocity-dependent dissipative term $-\frac{m\dot{\mathbf{r}}}{\tau}$.

$m\ddot{\mathbf{r}} = -e_0\boldsymbol{\mathcal{E}} - \frac{m\dot{\mathbf{r}}}{\tau}$ $\qquad$ (Newton's law for electron)

$\mathbf{r}(t) = \mathbf{r}_0 e^{-i\omega t}$ $\qquad$ (ansatz for electron position)

$\mathbf{r}_0 = \frac{e_0 \boldsymbol{\mathcal{E}}_0}{m\omega^2 + im\omega/\tau}$ $\qquad$ (corresponding amplitude)

$\implies \mathbf{r}(t) = \frac{e_0 \boldsymbol{\mathcal{E}}(t)}{m\omega^2 + im\omega/\tau}$

$\mathbf{j} = -n_e e_0 \mathbf{v}$ $\qquad$ (electric current density in general)

$= -n_e e_0 \frac{d}{dt}\left(\mathbf{r}_0 e^{-i\omega t}\right)$ $\qquad$ (using ansatz for $\mathbf{r}(t)$)

$= n_e e_0 \frac{i\omega e_0 \boldsymbol{\mathcal{E}}_0 e^{-i\omega t}}{m\omega^2 + im\omega/\tau}$ $\qquad$ (substituting in $\mathbf{r}_0$)

$= \frac{n_e e_0^2 \boldsymbol{\mathcal{E}}(t)}{m/\tau - im\omega}$ $\qquad$ (recognizing $\boldsymbol{\mathcal{E}}(t)$)

$= \frac{n_e e_0^2 \tau}{m}\frac{\boldsymbol{\mathcal{E}}(t)}{1 - i\omega\tau}$ $\qquad$ (result: Drude model current density)

Conductivity in an Alternating Electric Field

Goal: determine the Drude model's prediction for a metal's electric conductivity σ_E in an AC field.

$\mathbf{j}(t) = \frac{n_e e_0^2 \tau}{m}\frac{\boldsymbol{\mathcal{E}}(t)}{1 - i\omega\tau}$ $\qquad$ (review: current density in AC field)

$\mathbf{j} = \sigma_E \boldsymbol{\mathcal{E}}$ $\qquad$ (Ohm's law in general)

Compare to steady-state current density and conclude...

$\sigma_E = \frac{n_e e_0^2 \tau}{m(1 - i\omega\tau)}$ $\qquad$ (result: conductivity in an AC field)

Conductivity in a Steady DC Electric Field

Goal: determine the Drude model's prediction for a metal's electric conductivity σ_E in an steady-state DC field.

The steady state occurs when $\ddot{\mathbf{r}} = \mathbf{0}$

$\mathbf{0} = -e_0\boldsymbol{\mathcal{E}} - \frac{m\dot{\mathbf{r}}}{\tau}$ $\qquad$ (Newton's law in steady-state)

$\dot{\mathbf{r}} = -\frac{e_0 \tau}{m}\boldsymbol{\mathcal{E}}$ $\qquad$ (rearranging)

$\mathbf{j} = -n_e e_0 \dot{\mathbf{r}}$ $\qquad$ (current density in general)

$= \frac{n_e e_0^2 \tau}{m}\boldsymbol{\mathcal{E}}$ $\qquad$ (for steady-state velocity $\dot{\mathbf{r}}$)

$\mathbf{j} = \sigma_E \boldsymbol{\mathcal{E}}$ $\qquad$ (Ohm's law in general)

Compare to steady-state current density and conclude...

$$\sigma_{\mathrm{E}} = \frac{n_e e_0^2 \tau}{m}$$

(result: conductivity in steady DC field)

Shift of Fermi Sphere

Review: electron levels in a free electron gas at $T = 0\,\mathrm{K}$ are occupied up to the Fermi wave vector k_{F}

Consider electrons in a conductor exposed to an external electric field $\boldsymbol{\mathcal{E}}$.

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = -e_0 \boldsymbol{\mathcal{E}} \qquad \text{(Newton's law for a free electron)}$$

$$\hbar \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} = -e_0 \boldsymbol{\mathcal{E}} \qquad \text{(using } \mathbf{p} = \hbar\mathbf{k} \text{ for free electrons)}$$

$$\implies \mathbf{k}(t) = \mathbf{k}_0 - \frac{e_0 \boldsymbol{\mathcal{E}}}{\hbar} t$$

Conclusion: the Fermi sphere shifts in the direction of the external electric field with velocity $e_0\boldsymbol{\mathcal{E}}/\hbar$ (neglecting dissipative forces, which establish a steady state in time $\Delta t \sim \tau$).

$$\delta\mathbf{k} \sim -\frac{e_0\boldsymbol{\mathcal{E}}}{\hbar}\tau \qquad \text{(estimate for shift of Fermi sphere)}$$

In Passing: Mean Free Path

$$v_{\mathrm{F}} = \frac{\hbar k_{\mathrm{F}}}{m} \qquad \text{(Fermi velocity)}$$

$$\ell \sim v_{\mathrm{F}}\tau \qquad \text{(estimate for mean free path)}$$

Interpretation: ℓ is the average distance traveled between collisions by electrons near the Fermi surface

Experimental values in copper assuming $v_{\mathrm{F}} = 1.57 \cdot 10^6\,\mathrm{m\,s^{-1}}$

Temperature T	Mean free time τ	Mean free path ℓ
$4\,\mathrm{K}$	$2 \cdot 10^{-9}\,\mathrm{s}$	$0.3\,\mathrm{cm}$
$300\,\mathrm{K}$	$2 \cdot 10^{-14}\,\mathrm{s}$	$3 \cdot 10^{-6}\,\mathrm{cm}$

Electrons in a Periodic Potential

General goal: analyze the behavior of electrons in crystals.
Idea: crystal have periodic structure, so studying electron behavior in a periodic potential will help explain electron behavior in crystals.

General Considerations
Consider a crystal described by a Bravais lattice Λ with primitive vectors $\{\mathbf{a}_i\}$ and reciprocal primitive vectors $\{\mathbf{b}_i\}$
Fundamental assumption: the *potential $U(\mathbf{r})$ in the crystal shares the periodicity of the crystal's Bravais lattice.*
$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R})$ for all $\mathbf{R} \in \Lambda$ (**potential is periodic**)
Goal: find the single-electron energy eigenstates solving the stationary single-electron Schrödinger equation...
$$H\psi(\mathbf{r}) = \left[-\frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Bloch's Theorem

Bloch's theorem: solutions to the single-electron stationary Schrödinger equation in a periodic potential may be constructed to take the general form...
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \qquad (\textbf{Bloch wave function})$$

- n is a quantum number expressing energy band index

- $\mathbf{k}$ is a quantum number expressing electron wave vector
  $\mathbf{k}$ must satisfy the crystal's periodic BC, i.e.
  $$\mathbf{k} = \frac{n_x}{N_x}\mathbf{b}_x + \frac{n_y}{N_y}\mathbf{b}_y + \frac{n_z}{N_z}\mathbf{b}_z,\ n_i \in \mathbb{Z} \qquad (\text{PBC})$$

- $u_{n\mathbf{k}}$ is a function with periodicity of the crystal's Bravais lattice, i.e.
  $$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \qquad (u \text{ has period of BL})$$

Interpreting Bloch's theorem: electron wave functions in periodic potential are plane waves (as for free electrons) modulated by a periodic function $u_{n\mathbf{k}}$ (which encodes the effect of the crystal's potential).

Alternate Formulation of Bloch's Theorem
$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ (review: Bloch wave function)
$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$
$\qquad = e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} u_{n\mathbf{k}}(\mathbf{r})$ (since $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) \equiv u_{n\mathbf{k}}(\mathbf{r})$)
$\qquad = e^{i\mathbf{k}\cdot\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ (rearranging)
$\qquad = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$ (recognizing original $\psi_{n\mathbf{k}}$)
Conclusion: an equivalent formulation of Bloch's theorem reads: solutions to the single-electron Schrödinger equation in a periodic potential may be constructed so that associated with each solution ψ is a wave vector $\mathbf{k}$ for which
$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi(\mathbf{r})\ \forall\ \mathbf{R} \in \Lambda$ (alternate Bloch's theorem)

Proof of Bloch's Theorem Using Translation Operators
Consider a crystal described by a Bravais lattice Λ with primitive vectors $\{\mathbf{a}_i\}$ and reciprocal primitive vectors $\{\mathbf{b}_i\}$
$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R})$ for all $\mathbf{R} \in \Lambda$ (potential is periodic)
$H = -\frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r})$ (electron Hamiltonian)
$H(\mathbf{r} + \mathbf{R}) = H(\mathbf{r})$ (since $U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R})$)

Hamiltonian and Translation Operator Commute
$\mathbf{T_R}\, f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$ (def. of translation operator $\mathbf{T_R}$)
$\mathbf{T_R}\, H(\mathbf{r})\psi = H(\mathbf{r} + \mathbf{R})\mathbf{T_R}\,\psi$
$\qquad = H(\mathbf{r})\mathbf{T_R}\,\psi$ (using $H(\mathbf{r}+\mathbf{R}) = H(\mathbf{r})$)
$\implies \mathbf{T_R}\, H = H\mathbf{T_R}$ ($\mathbf{T_R}$, H commute)
Result: since $\mathbf{T_R}$ and H commute, eigenstates of H can be chosen to also be eigenstates of $\mathbf{T_R}$.
$H\psi = E\psi$ (eigenvalue equation for H)
$\mathbf{T_R}\,\psi = c(\mathbf{R})\psi$ (eigenvalue equation for $\mathbf{T_R}$)

Lemma For $\mathbf{T_R}$ Eigenvalues
$\mathbf{T_R}\,\mathbf{T_{R'}}\,\psi(\mathbf{r}) = \mathbf{T_{R'}}\,\mathbf{T_R}\,\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R} + \mathbf{R'})$
$\implies \mathbf{T_{R'}}\,\mathbf{T_R} = \mathbf{T_R}\,\mathbf{T_{R'}} = \mathbf{T_{R+R'}}$
$\mathbf{T_{R'}}\,\mathbf{T_R}\,\psi = c(\mathbf{R})\mathbf{T_{R'}}\,\psi = c(\mathbf{R})c(\mathbf{R'})\psi$ (result I)
$\qquad = \mathbf{T_{R+R'}}\,\psi$ (using $\mathbf{T_{R'}}\,\mathbf{T_R} = \mathbf{T_{R+R'}}$)
$\qquad = c(\mathbf{R} + \mathbf{R'})\psi$ (result II)
$\implies c(\mathbf{R})c(\mathbf{R'}) = c(\mathbf{R} + \mathbf{R'})$ (combining I and II)

Completing the Proof
$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,\ n_j \in \mathbb{Z}$ (review: general BL vector)
$c(\mathbf{R} + \mathbf{R'}) = c(\mathbf{R})c(\mathbf{R'})$ (review: $\mathbf{T_R}$ eigenvalue identity)
Write translation operator eigenvalues for primitive vectors $\{\mathbf{a}_j\}$ in the general form...
$c(\mathbf{a}_j) = e^{2\pi i x_j},\ x_j \in \mathbb{C}$ (eigval. for primitive vectors)
$c(\mathbf{R}) = c(n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3)$ (substituting in $\mathbf{R}$)
$\qquad = c(n_1\mathbf{a}_1)c(n_2\mathbf{a}_2)c(n_3\mathbf{a}_3)$ (using $\mathbf{T_R}$ eigval identity)
$\qquad = e^{2\pi i(n_1 x_1 + n_2 x_2 + n_3 x_3)}$ (using $c(\mathbf{a}_j) = e^{2\pi i x_i}$)
Next, consider an arbitrary RL vector of the form....
$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$
$i\mathbf{k}\cdot\mathbf{R} = 2\pi i(n_1 x_1 + n_2 x_2 + n_3 x_3)$ (using $\mathbf{a}_i\mathbf{b}_j = 2\pi\delta_{ij}$)
Compare to $c(\mathbf{R}) = e^{2\pi i(n_1 x_1 + n_2 x_2 + n_3 x_3)}$ to conclude...
$c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}$ for $\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$
$c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}$ (general form of $\mathbf{T_R}$ eigenvalue)
$\psi(\mathbf{r} + \mathbf{R}) = \mathbf{T_R}\,\psi(\mathbf{r}) = c(\mathbf{R})\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$
Compare first and last term of equality to conclude...
$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$ (result: Bloch's theorem)

Bloch's Theorem: Quantization of k Space
Goal: show how the Sommerfeld free electron expressions for quantization of $\mathbf{k}$ space transfer to Bloch electrons.

Review: Periodic Boundary Conditions
As for free electrons, we will impose periodic boundary conditions on Bloch electron wave functions. Reviewing from Periodic Boundary Conditions, consider a crystal with...

- side lengths L_1, L_2, L_3,

- lattice constants a_1, a_2, a_3,

- number of lattice sites N_1, N_2, N_3,

- primitive vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, and

- reciprocal primitive vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$...

$L_i = N_i a_i$ (relating lattice constant and crystal length)
Let $\mathbf{L}_i \equiv N_i\mathbf{a}_i$ (vector side length)
$N = N_1 N_2 N_3$ (total number of lattice sites)
$\psi_{n\mathbf{k}}(x, y, z) \equiv \psi_{n\mathbf{k}}(x + L_1, y + L_2, z + L_3)$ (**PBC**)
$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{L}_i) \equiv \psi_{n\mathbf{k}}(\mathbf{r}),\ i = 1, 2, 3$ (in vector form)
$\psi_{n\mathbf{k}}(\mathbf{r} + N_i\mathbf{a}_i) \equiv \psi_{n\mathbf{k}}(\mathbf{r}),\ i = 1, 2, 3$ (in terms of N_i and $\mathbf{a}_i$)

Bloch's Theorem and Periodic Boundary Conditions
Goal: derive the general expression for Bloch wave vectors $\mathbf{k}$ allowed under periodic boundary conditions.
$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r})$ (review: Bloch's theorem)
$\psi_{n\mathbf{k}}(\mathbf{r} + N_j\mathbf{a}_j) = e^{iN_j\mathbf{k}\cdot\mathbf{a}_j}\psi_{n\mathbf{k}}(\mathbf{r})$ (letting $\mathbf{R} = N_j\mathbf{a}_j$)
Compare to PBC $\psi_{n\mathbf{k}}(\mathbf{r} + N_j\mathbf{a}_j) \equiv \psi_{n\mathbf{k}}(\mathbf{r})$ to conclude....
$e^{iN_j\mathbf{k}\cdot\mathbf{a}_j} = 1,\ j = x, y, z$
$\implies N_j\mathbf{k}\cdot\mathbf{a}_j = 2\pi m_j,\ m_j \in \mathbb{Z}$ (to satisfy $e^{iN_j\mathbf{k}\cdot\mathbf{a}_j} = 1$)
$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$ (general Bloch wave vector)
Substitute $\mathbf{k} = \sum_i x_i\mathbf{b}_i$ into $N_j\mathbf{k}\cdot\mathbf{a}_j = 2\pi m_j$ to get...
$2\pi m_j = N_j\left(\sum_i x_i\mathbf{b}_i\right)\cdot\mathbf{a}_j$
$\qquad = 2\pi N_j x_j$ (using $\mathbf{a}_i\cdot\mathbf{b}_j = 2\pi\delta_{ij}$)
$\implies x_j = \frac{m_j}{N_j}$ (solving for x_j)
Substitute $x_j = m_j/N_j$ into $\mathbf{k} = \sum_j x_j\mathbf{b}_j$ to get...

$$\mathbf{k} = \sum_j \frac{m_j}{N_j}\mathbf{b}_j, \;\; m_j \in \mathbb{Z} \qquad \text{(result: a general Bloch WV)}$$

Allowed Bloch Wave Vectors Per RL PUC

Goal: determine the number of allowed Bloch wave vectors $\mathbf{k}$ in a single reciprocal primitive unit cell.

$\mathbf{k} = \sum_j \frac{m_j}{N_j}\mathbf{b}_j \qquad$ (review: general Bloch WV)

$\implies$ the smallest allowed spacing between discrete $\mathbf{k}$ occur for $m_1 = m_2 = m_3 = 1$, so the smallest region of $\mathbf{k}$-space allowed per $\mathbf{k}$ is a parallelepiped spanned by vectors $\mathbf{b}_j/N_j$.

$$\Delta\mathbf{k} = \left| \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right) \right| \qquad \text{(k-space volume per allowed k)}$$
$$= \frac{1}{N}|\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)| \qquad \text{(using } N = N_1 N_2 N_3)$$
$$= \frac{V_0^*}{N} \qquad \text{(recognizing volume of RL primitive unit cell)}$$

Idea: the number $N_\mathbf{k}$ of allowed $\mathbf{k}$ in a RL primitive unit cell is the volume V_0^* of the PUC divided by the volume $\Delta\mathbf{k}$ per allowed $\mathbf{k}$, i.e.

$N_\mathbf{k} = \frac{V_0^*}{\Delta\mathbf{k}} = N \qquad$ (result: number of $\mathbf{k}$ per RL PUC)

Result: the number of allowed $\mathbf{k}$ per reciprocal lattice PUC equals the number of lattice sites in the crystal.

Volume Per Bloch Electron Wave Vector

Goal: determine how many allowed values of electron wave vector $\mathbf{k}$ are contained per unit volume of $\mathbf{k}$ space in crystal of volume V for Bloch electrons.

Consider a crystal of volume V with N lattice sites, direct lattice primitive unit cell volume $V_0 = V/N$ and reciprocal lattice PUC volume $V_0^* = (2\pi)^3/V_0$.

$\Delta\mathbf{k} = \frac{V_0^*}{N} \qquad$ (review: $\mathbf{k}$-space volume per allowed $\mathbf{k}$)

$V_0^* = \frac{(2\pi)^3}{V_0} = (2\pi)^3 \frac{N}{V} \qquad$ (review: volume of RL PUC)

Combine $\Delta\mathbf{k} = \frac{V_0^*}{N}$ and $V_0^* = (2\pi)^3 N/V$ to get...

$\Delta\mathbf{k} = \frac{(2\pi)^3}{V} \qquad$ (result: volume per Bloch WV)

Conclusion: the $\mathbf{k}$-space volume per Bloch electron wave vector equals the $\mathbf{k}$-space volume per free electron wave vector derived in Quantization of $\mathbf{k}$ Space.

Proof of Bloch's Theorem by Explicit Construction

Consider a crystal described by a Bravais lattice Λ with primitive vectors $\{\mathbf{a}_i\}$ and reciprocal primitive vectors $\{\mathbf{b}_i\}$.

Plan: explicitly derive that solutions to the single-electron Schrödinger equation may be written in the form...

$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}), \;\; u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$

Assumptions:

- ψ satisfies periodic boundary conditions, i.e.
  $\psi(\mathbf{r}+N_i\mathbf{a}_i) = \psi(\mathbf{r}), \;\; i = 1,2,3 \qquad (\psi \text{ obeys PBC})$

- The potential U has the periodicity of the BL, i.e.
  $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r}) \qquad (U \text{ has lattice periodicity})$

- General Bloch wave vectors satisfy periodic boundary
  $\mathbf{k} = \frac{m_1}{N_1}\mathbf{b}_1 + \frac{m_2}{N_2}\mathbf{b}_2 + \frac{m_3}{N_3}\mathbf{b}_3, \;\; m_j \in \mathbb{Z}$ (general Bloch WV)

Ansatzes For Wave Function and Potential

Concept: since the electron wave function ψ satisfies the crystal's PBC, ψ may be expanded over a basis of plane waves with Bloch wave vectors obeying the PBC, i.e.

$\psi(\mathbf{r}) = \sum_\mathbf{q} c_\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}}, \qquad$ (ansatz for e^- wave function)

Concept: since the potential U has the periodicity of the lattice, U may be expanded over a basis of plane waves with reciprocal lattice vectors

$U(\mathbf{r}) = \sum_\mathbf{K} U_\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{r}} \qquad$ (ansatz for potential)

$U(\mathbf{r}+\mathbf{R}) = \sum_\mathbf{K} U_\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{r}} e^{i\mathbf{K}\cdot\mathbf{R}}$
$= \sum_\mathbf{K} U_\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{r}} \qquad$ (since $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$)

$= U(\mathbf{r}) \qquad$ (satisfying $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$)

Conclusion: ansatz for U satisfies lattice periodicity.

Interpreting the Potential Ansatz

$U(\mathbf{r}) = \sum_\mathbf{K} U_\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{r}} \qquad$ (review: potential ansatz)

Mathematical interpretation: $U(\mathbf{r})$ is an inverse discrete Fourier transform of U from reciprocal to position space.

$U_\mathbf{K} = \frac{1}{V_0} \iiint_\text{cell} U(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}\, dV \qquad$ (Fourier components)

V_0 is the volume of a single unit cell

$U_{\mathbf{K}=0} \equiv 0 \quad$ (by convention, since potential offset is arbitrary)

$U_\mathbf{K}^* = U_{-\mathbf{K}} \qquad\qquad$ (if $U(\mathbf{r})$ is real)

$U_\mathbf{K} = U_{-\mathbf{K}} \qquad\qquad$ (if $U(\mathbf{r})$ is even)

$U_\mathbf{K}^* = U_\mathbf{K} \implies U_\mathbf{K} \in \mathbb{R} \qquad$ (if $U(r)$ is real and even)

Solving the Schrödinger Equation I

$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad$ (review: Schrödinger eq.)

$\psi(\mathbf{r}) = \sum_\mathbf{q} c_\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}} \qquad$ (review: ansatz for e^- wave function)

$U(\mathbf{r}) = \sum_\mathbf{K} U_\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{r}} \qquad$ (review: ansatz for potential)

$U_\mathbf{K} = \frac{1}{V_0}\iiint_\text{cell} U(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}\,dV \qquad$ (review: Fourier modes)

Substitute ansatzes for ψ and U into Schrödinger eq. to get...

$\nabla^2\psi = \nabla^2 \sum_\mathbf{q} c_\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}} = -\sum_\mathbf{q} q^2 c_\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}} \qquad$ (aux. calculation)

$\psi(\mathbf{r})U(\mathbf{r}) = \sum_{\mathbf{K}\mathbf{q}} c_\mathbf{q} U_\mathbf{K} e^{i(\mathbf{K}+\mathbf{q})\cdot\mathbf{r}} \qquad$ (auxiliary calculation)

$= \sum_{\mathbf{K}\mathbf{q}'} c_{\mathbf{q}'} U_\mathbf{K} e^{i(\mathbf{K}+\mathbf{q}')\cdot\mathbf{r}} \qquad$ (re-indexing $\mathbf{q} \to \mathbf{q}'$)

$= \sum_{\mathbf{K}\mathbf{q}} c_{\mathbf{q}-\mathbf{K}} U_\mathbf{K} e^{i\mathbf{q}\cdot\mathbf{r}} \qquad$ (new var. $\mathbf{q} \equiv \mathbf{K}+\mathbf{q}'$)

Substitute auxiliary calculations into Sch. equation to get...

$\frac{\hbar^2}{2m}\sum_\mathbf{q} c_\mathbf{q} q^2 e^{i\mathbf{k}\cdot\mathbf{q}} + \sum_{\mathbf{K},\mathbf{q}} c_{\mathbf{q}-\mathbf{K}} U_\mathbf{K} e^{i\mathbf{q}\cdot\mathbf{r}} = E\sum_\mathbf{q} c_\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}} \quad$ (Sch. eq.)

$\sum_\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}}\left(\frac{\hbar^2 q^2}{2m}c_\mathbf{q} + \sum_\mathbf{K} c_{\mathbf{q}-\mathbf{K}}U_\mathbf{K} \right) = \sum_\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}}c_\mathbf{q}E \qquad$ (factoring)

Idea: both sides are sums over *orthogonal*, linearly-independent plane wave terms $\implies$ summands must be equal for the equation to hold for arbitrary values of $\mathbf{q}$.

$\frac{\hbar^2 q^2}{2m}c_\mathbf{q} + \sum_\mathbf{K} c_{\mathbf{q}-\mathbf{K}}U_\mathbf{K} = c_\mathbf{q}E \qquad$ (equating summands over $\mathbf{q}$)

$\left(\frac{\hbar^2 q^2}{2m} - E \right)c_\mathbf{q} + \sum_\mathbf{K} c_{\mathbf{q}-\mathbf{K}}U_\mathbf{K} = 0 \qquad$ (rearranged)

Interpretation: above result is a homogeneous system of coupled linear equations for the coefficients $c_\mathbf{q}$ needed to find ψ.

Intermezzo: Plane Waves are Orthogonal

Goal: justifying equating summands in the previous step by showing that plane waves of the form $e^{i\mathbf{q}\cdot\mathbf{r}}$, with $\mathbf{q}$ satisfying the crystal's PBC, are orthogonal, i.e. that...

$$\iiint_V e^{i\mathbf{q}\cdot\mathbf{r}} = \begin{cases} 0 & \mathbf{q} \text{ satisfies PBC} \\ 1 & \mathbf{q} = \mathbf{0} \\ \text{irrelevant} & \text{otherwise} \end{cases}$$

Shift original crystal volume V with origin at $\mathbf{r} = \mathbf{0}$ to new region V' with origin at $\mathbf{r} = \mathbf{d}$

$\iiint_V e^{i\mathbf{q}\cdot\mathbf{r}}\,dV = \iiint_{V'} e^{i\mathbf{q}(\mathbf{r}+\mathbf{d})}\,dV$

$= \iiint_V e^{i\mathbf{q}(\mathbf{r}+\mathbf{d})}\,dV \qquad$ (by PBC imposed on $\mathbf{q}$)

$(1 - e^{i\mathbf{q}\cdot\mathbf{d}})\iiint_V e^{i\mathbf{q}\cdot\mathbf{r}}\,dV = 0 \qquad$ (rearranged)

$\implies$ for the equation to hold for all $\mathbf{d}$, we conclude...

$$\iiint_V e^{i\mathbf{q}\cdot\mathbf{r}} = \begin{cases} 0 & \mathbf{q} \text{ satisfies PBC} \\ 1 & \mathbf{q} = \mathbf{0} \end{cases}$$

The Restricted Zone Scheme

$\left(\frac{\hbar^2 q^2}{2m} - E \right)c_\mathbf{q} + \sum_\mathbf{K} U_\mathbf{K} c_{\mathbf{q}-\mathbf{K}} = 0 \qquad$ (for review)

Key idea: *for each wave vector $\mathbf{q}$ that falls outside the first Brillioun zone, there exists a reciprocal lattice vector $\mathbf{K}$ such that $\mathbf{k} = \mathbf{q} + \mathbf{K}$ lies in the first Brillioun zone.*

$\implies$ each $\mathbf{q}$ can be equivalently expressed as $\mathbf{q} = \mathbf{k} - \mathbf{K}$.

Expressing $\mathbf{q}$ in terms of $\mathbf{k}$ in the first Brillouin zone and a RL vector $\mathbf{K}$ is called the *restricted zone scheme*.

Solving the Schrödinger Equation II
Plan: express system of equations for $c_{\mathbf{q}}$ only in terms of $\mathbf{k}$ in the crystal's first BZ, i.e. using restricted zone scheme.

$$\left(\frac{\hbar^2 q^2}{2m} - E\right) c_{\mathbf{q}} + \sum_{\mathbf{K}} U_{\mathbf{K}} c_{\mathbf{q}-\mathbf{K}} = 0 \qquad \text{(for review)}$$

$$\left(\frac{\hbar^2 q^2}{2m} - E\right) c_{\mathbf{q}} + \sum_{\mathbf{K}} U_{\mathbf{K}} c_{\mathbf{q}-\mathbf{K}} = 0 \qquad \text{(in terms of } \mathcal{E}_{\mathbf{q}}^{(0)}\text{)}$$

$$\left(\frac{\hbar^2 q^2}{2m} - E\right) c_{\mathbf{q}} + \sum_{\mathbf{K}''} U_{\mathbf{K}''} c_{\mathbf{q}-\mathbf{K}''} = 0 \qquad \text{(re-indexing)}$$

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{K})^2 - E\right] c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}''} U_{\mathbf{K}''} c_{\mathbf{k}-\mathbf{K}-\mathbf{K}''} = 0 \qquad (\mathbf{q} \to \mathbf{k}-\mathbf{K})$$

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{K})^2 - E\right] c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0 \qquad (\mathbf{K}+\mathbf{K}'' \to \mathbf{K}')$$

Interpretation: above result is a homogeneous system of coupled linear equations for the coefficients $c_{\mathbf{q}}$ needed to find ψ, with $\mathbf{q}$ expressed as $\mathbf{q} = \mathbf{k} - \mathbf{K}$ via restricted zone scheme.

Completing Construction of Bloch's Theorem
Summary: using plane wave ansatzes, the Sch. eq. reduces to
$$\left[\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{K})^2 - E\right] c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0$$
Key concept: the above system equations couples only those coefficients $c_{\mathbf{k}-\mathbf{K}'}$ separated by reciprocal lattice vectors $\mathbf{K}'$.
Result: the Schrödinger equation for Bloch electrons decomposes into N *independent* problems for each $\mathbf{k}$ in the crystal's first Brillouin zone.
Each solution (for a given $\mathbf{k}$) is indexed by an additional quantum number $n \in \mathbb{N}$ ranging from 0 to ∞ (like a hydrogen atom's principal quantum number.)
The electron wave function ansatz thus simplifies to...

$$\psi_{n\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}}^{(n)} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}} \qquad \text{(simplified } e_- \text{ wave function)}$$

$$= e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}}^{(n)} e^{-i\mathbf{K}\cdot\mathbf{r}} \qquad \text{(factoring out } e^{i\mathbf{k}\cdot\mathbf{r}}\text{)}$$

Let $u_{n\mathbf{k}}(\mathbf{r}) \equiv \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}}^{(n)} e^{-i\mathbf{K}\cdot\mathbf{r}}$ to get...

$$\psi_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \qquad \text{(result: Bloch's theorem)}$$

Generalized Density of Levels
Goal: generalize expression for free electron density of levels to nearly-free electrons in a weak periodic potential.

Implicit Definition of Generalized DOL
Let $Q_n = Q_n\big(E_n(\mathbf{k})\big)$ be a function of electron energy
Let Q denote the weighted sum of Q_n over all electron levels...

$$Q = 2 \sum_{n,\mathbf{K}} Q_n\big(E_n(\mathbf{k})\big) \qquad \text{(factor of 2 from } e^- \text{ spin)}$$

$$q = \frac{2}{V} \sum_{n,\mathbf{K}} Q_n\big(E_n(\mathbf{k})\big) \qquad \text{(volume-normalized)}$$

$$= \frac{2}{V} \frac{1}{\Delta\mathbf{k}} \sum_{n,\mathbf{K}} Q_n\big(E_n(\mathbf{k})\big)\Delta\mathbf{k} \qquad \text{(dividing/multiplying by } \Delta\mathbf{k}\text{)}$$

$$\approx \frac{2}{V} \frac{V}{(2\pi)^3} \sum_n \iiint Q_n\big(E_n(\mathbf{k})\big) \, d^3\mathbf{k} \qquad \text{(using } \Delta\mathbf{k} = \frac{(2\pi^3)}{V}\text{)}$$

$$\approx \frac{1}{4\pi^3} \sum_n \iiint Q_n\big(E_n(\mathbf{k})\big) \, d^3\mathbf{k} \qquad \text{(simplifying)}$$

If q depends on n and $\mathbf{k}$ only through $E_n(\mathbf{k})$, we may define....

$$q = \int g(E)Q(E) \, dE \qquad \text{(defining density of levels } g(E)\text{)}$$

$$\int g(E)Q(E) \, dE = q = \sum_n \iiint Q_n\big(E_n(\mathbf{k})\big)\frac{d^3\mathbf{k}}{4\pi^3} \qquad \text{(equating } q\text{)}$$

DOL in a Fixed Energy Band
$$\int g(E)Q(E) \, dE = \sum_n \iiint Q_n\big(E_n(\mathbf{k})\big)\frac{d^3\mathbf{k}}{4\pi^3} \qquad \text{(for review)}$$

Comparing LHS and RHS of above equality motivates...
$$g(E) \equiv \sum_n g_n(E) \qquad \text{(summed over energy bands)}$$

$$g_n(E) \equiv \iiint \delta\big(E - E_n(\mathbf{k})\big)\frac{d^3\mathbf{k}}{4\pi^3} \qquad \textbf{(DOL in } n\textbf{-th band)}$$

Rationale: precisely this definition of $g_n(E)$ preserves the defi-nition of the generalized density of levels.

<u>Proof:</u>
Substitute $g_n(E)$ into $g(E)$ to get...
$$g(E) = \frac{1}{4\pi^3} \sum_n \iiint \delta\big(E - E_n(\mathbf{k})\big) \, d^3\mathbf{k}$$
Substitute $g(E)$ into integral definition of q to get...
$$q = \int g(E)Q(E) \, dE$$
$$= \int \left\{ \sum_n \left[\iiint \delta\big(E - E_n(\mathbf{k})\big)\frac{d^3\mathbf{k}}{4\pi^3} \right] Q(E) \right\} dE$$
$$= \sum_n \iiint \left[\int \delta\big(E - E_n(\mathbf{k})\big)Q(E) \, dE \right] \frac{d^3\mathbf{k}}{4\pi^3} \qquad \text{(rearranged)}$$
$$= \sum_n \iiint Q_n\big(E_n(\mathbf{k})\big)\frac{d^3\mathbf{k}}{4\pi^3} \qquad \text{(by def. of } \delta \text{ function)}$$
...which agrees with the summation expression for q used in the implicit definition of the generalized DOL.

Fixed-Band DOL in Terms of Gradient
Goal: derive an explicit relationship between $E_n(\mathbf{k})$ and $g_n(E)$
$$g_n(E) = \iiint \delta\big(E - E_n(\mathbf{k})\big)\frac{d^3\mathbf{k}}{4\pi^3} \qquad \text{(review: DOL in } n\text{-th band)}$$
Goal: find the allowed $\mathbf{k}$ for which $E_n(\mathbf{k}) \in (E, E + dE)$.
$$g_n(E) \, dE = \begin{cases} \iiint \frac{d^3\mathbf{k}}{4\pi^3} & E_n(\mathbf{k}) \in (E, E+dE) \\ 0 & \text{otherwise} \end{cases}$$
Consider the following ideas...

- Let $S_n(E)$ denote the surface in $\mathbf{k}$ space of constant energy $E_n(\mathbf{k}) = E$ in the n-th energy band.

- The $\mathbf{k}$ for which $E_n(\mathbf{k}) \in (E, E + dE)$ fall in the region of $\mathbf{k}$-space bounded by $S_n(E)$ and $S_n(E + dE)$.

- Idea: since dE is infinitesimal, $g_n(E) \, dE$ may we written as a surface integral.

Combine above three ideas to write $g_n(E) \, dE$ as...
$$g_n(E) \, dE = \iint_{S_n(E)} \frac{\delta\mathbf{k}}{4\pi^3} \cdot d\mathbf{S}$$
$$\equiv \iint_{S_n(E)} \frac{\delta k_\perp}{4\pi^3} \, dS$$
$\delta k_\perp$ is the component of $\delta\mathbf{k}$ normal to the surface $S_n(E)$

$$dE = \nabla E_n(\mathbf{k}) \cdot \delta\mathbf{k} \qquad \text{(the differential } dE \text{ in general)}$$
Recall $\nabla E_n(\mathbf{k})$ is normal to surfaces of constant E to get...
$$dE = |\nabla E_n(\mathbf{k})|\delta k_\perp \qquad \text{(evaluating dot product)}$$
$$\implies \delta k_\perp = \frac{dE}{|\nabla E_n(\mathbf{k})|} \qquad \text{(solving for } \delta k_\perp\text{)}$$
Substitute $\delta k_\perp$ into surface integral for $g_n(E) \, dE$ to get...
$$g_n(E) \, dE = \frac{1}{4\pi^3} \iint_{S_n(E)} \frac{dS}{|\nabla E_n(\mathbf{k})|} \, dE$$
Finally, cancel dE from both sides to get...
$$g_n(E) = \frac{1}{4\pi^3} \iint_{S_n(E)} \frac{dS}{|\nabla E_n(\mathbf{k})|} \qquad \textbf{(gen. DOL in } n\textbf{-th band)}$$

Nearly-Free Electron Model
Model: Assume Bloch electrons are nearly free; model Bloch wave function as a free electron plane wave perturbed by the crystal's (weak) periodic potential.
The NFEM applies to metals with s or p orbitals outside a closed-shell noble gas configuration (e.g. groups I, II, III, IV).

General Considerations
Model Bloch wave function as expansion over plane waves
$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}} \qquad \text{(NFEM ansatz)}$$
Wave function coefficients $c_{\mathbf{k}-\mathbf{K}}$ and energies E are found by solving the eigenvalue problem...
$$\left[\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{K})^2 - E\right] c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0$$
$$U_{\mathbf{K}} = \frac{1}{V_0} \iiint_{\text{cell}} U(\mathbf{r})e^{-\mathbf{K}\cdot\mathbf{r}} \, dV \qquad \text{(review: Fourier components)}$$
Shorthand: let $E_{\mathbf{k}}^{(0)} \equiv \frac{\hbar^2}{2m}k^2 \qquad \text{(free electron energy)}$
$$\left(E_{\mathbf{k}-\mathbf{K}}^{(0)} - E\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0 \qquad \text{(in terms of } E_{\mathbf{k}}^{(0)}\text{)}$$

Limit Case: Free Electrons
Goal: analyze the NFEM for completely free electrons.

$U_{\mathbf{K}} = 0$ for all $\mathbf{K}$ $\qquad$ (for free electrons with $U(\mathbf{r}) = 0$)

$\left(E^{(0)}_{\mathbf{k}-\mathbf{K}} - E\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0$ $\qquad$ (in general)

$\left(E^{(0)}_{\mathbf{k}-\mathbf{K}} - E\right) c_{\mathbf{k}-\mathbf{K}} = 0$ $\qquad$ (for free electrons)

Conclusion: In limit of free electrons, for each $\mathbf{K}$, either

(a) $E = E^{(0)}_{\mathbf{k}-\mathbf{K}}$ $\qquad$ (Bloch e^- have free e^- energy)

(b) $c_{\mathbf{k}-\mathbf{K}} = 0$ $\qquad$ (the level $\mathbf{k} - \mathbf{K}$ doesn't contribute to $\psi_{\mathbf{k}}$)

More so, $E = E^{(0)}_{\mathbf{k}-\mathbf{K}}$ can occur...

(a) for a single $\mathbf{K} = \mathbf{K}_0$, giving the non-degenerate solution
$E = E^{(0)}_{\mathbf{k}-\mathbf{K}}$ $\qquad$ (energy)
$\psi_{\mathbf{k}} \propto e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}$ $\qquad$ (wave function)

(b) for multiple $\mathbf{K} = \mathbf{K}_1, \ldots, \mathbf{K}_m$, giving the degenerate solution
$E = E_{\mathbf{k}-\mathbf{K}_1} = \cdots = E_{\mathbf{k}-\mathbf{K}_m}$ $\qquad$ (energy)
$\psi_{\mathbf{k}} \propto a_1 e^{i(\mathbf{k}-\mathbf{K}_1)\cdot\mathbf{r}} + \cdots + a_m e^{i(\mathbf{k}-\mathbf{K}_m)\cdot\mathbf{r}}$ $\qquad$ (wave function)

NFEM: Typical Analysis Procedure

1. Choose a fixed $\mathbf{k}$ in the first Brillioun zone

2. Find the finite set of m reciprocal vectors $\{\mathbf{K}'\}$ for which $E_{\mathbf{k}-\mathbf{K}'}$ is a degenerate solution

3. For the chosen wave vector $\mathbf{k}$ and each $\mathbf{K} \in \{\mathbf{K}'\}$, solve the $m \times m$ homogeneous system
$\left(E^{(0)}_{\mathbf{k}-\mathbf{K}} - E\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0$
to get m eigenvalues $\{E_{n\mathbf{k}}\}$ and eigenvectors $\mathbf{c}^{(n)}_{\mathbf{k}} \in \mathbb{C}^m$
$\mathbf{c}^{(n)}_{\mathbf{k}} = (c^{(n)}_{\mathbf{k}-\mathbf{K}_1}, \ldots, c^{(n)}_{\mathbf{k}-\mathbf{K}_m})$ $\qquad$ (eigenvector elements)

4. Arrange eigenvalue-eigenvector pairs in order of increasing energy, indexed by the quantum number n. The quantum number n is called the *energy band index*.

The NFEM wave function of a Bloch electron with wave vector $\mathbf{k}$ and band index n is then...
$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c^{(n)}_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}$ $\qquad$ (**NFEM wave function**)

Weak Potential and Nondegenerate Solution

For a fixed wave vector $\mathbf{k}$, consider a reciprocal lattice vector $\mathbf{K}_0$ with nondegenerate free electron energy $E = E^{(0)}_{\mathbf{k}-\mathbf{K}_0}$.
$E - E^{(0)}_{\mathbf{k}-\mathbf{K}_0} = 0$ $\qquad$ (free e^- nondegenerate energy)

Concept: for a weak potential $U(\mathbf{r})$, the condition that $E^{(0)}_{\mathbf{k}-\mathbf{K}}$ be nondegenerate generalizes to...
$\left|E^{(0)}_{\mathbf{k}-\mathbf{K}} - E^{(0)}_{\mathbf{k}-\mathbf{K}_0}\right| \gg U_{\mathbf{K}'}$ for all $\mathbf{K} \neq \mathbf{K}_0$ and $U_{\mathbf{K}'}$

Interpretation: the free electron energy $E^{(0)}_{\mathbf{k}-\mathbf{K}_0}$ is very far from all other free electron energies on the scale of a typical Fourier component $U_{\mathbf{K}'}$.
Goal: analyze how the presence of a weak potential perturbs the non-degenerate free electron level with energy $E^{(0)}_{\mathbf{k}-\mathbf{K}_0}$.

Analysis

Consider the non-degenerate free e^- level $E^{(0)}_{\mathbf{k}-\mathbf{K}_0}$.
$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}$ $\qquad$ (review: NFEM ansatz)

$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}}\right) c_{\mathbf{k}-\mathbf{K}} = \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}}$ $\qquad$ (review: NFEM eqs.)

$c_{\mathbf{k}-\mathbf{K}} \sim \begin{cases} 1 & \mathbf{K} = \mathbf{K}_0 \\ 0 & \text{otherwise} \end{cases}$ $\qquad$ (for a nondegenerate level)

Interpretation: assume only the plane wave $e^{i(\mathbf{k}-\mathbf{K}_0)\cdot\mathbf{r}}$ contributes appreciably to the nondegenerate solution.

Approximate Expression for Coefficients

Goal: find approximate expression for $c_{\mathbf{k}-\mathbf{K}}$ for weak potential and non-degenerate level with $\mathbf{K} = \mathbf{K}_0$.

$c_{\mathbf{k}-\mathbf{K}} \sim \begin{cases} 1 & \mathbf{K} = \mathbf{K}_0 \\ 0 & \text{otherwise} \end{cases}$ $\qquad$ (for a nondegenerate level)

$\implies \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} \approx c_{\mathbf{k}-\mathbf{K}_0} U_{\mathbf{K}_0-\mathbf{K}}$ $\qquad$ (for a ndg. level)

Substitute this sum into general NFEM system of eq. to get...
$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}'}\right) c_{\mathbf{k}-\mathbf{K}'} \approx c_{\mathbf{k}-\mathbf{K}_0} U_{\mathbf{K}_0-\mathbf{K}'}$ $\qquad$ (for a ndg. level)

Solve for $c_{\mathbf{k}-\mathbf{K}'}$ and reindex $\mathbf{K}' \to \mathbf{K}$ to get...
$\implies c_{\mathbf{k}-\mathbf{K}} \approx \frac{c_{\mathbf{k}-\mathbf{K}_0} U_{\mathbf{K}_0-\mathbf{K}}}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}}$ $\qquad$ (result: $c_{\mathbf{k}}$ for ndg. level)

Solving for Energy

Solve system of NFEM eqs. with chosen $\mathbf{K} = \mathbf{K}_0$, giving...
$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_0}\right) c_{\mathbf{k}-\mathbf{K}_0} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_0}$ $\qquad$ (for $\mathbf{K} = \mathbf{K}_0$)

$= \sum_{\mathbf{K}\neq\mathbf{K}_0} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_0}$ $\qquad$ (since $U_{\mathbf{0}} = 0$)

$\approx \sum_{\mathbf{K}\neq\mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} U_{\mathbf{K}_0-\mathbf{K}}}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}} U_{\mathbf{K}-\mathbf{K}_0}$ $\qquad$ (ndg. $c_{\mathbf{k}-\mathbf{K}}$)

$\approx \sum_{\mathbf{K}\neq\mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} \left|U_{\mathbf{K}-\mathbf{K}_0}\right|^2}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}}$ $\qquad$ ($U^*_{\mathbf{K}} = U_{-\mathbf{K}}$)

$E = E^{(0)}_{\mathbf{k}-\mathbf{K}_0} + \sum_{\mathbf{K}\neq\mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} \left|U_{\mathbf{K}-\mathbf{K}_0}\right|^2}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}}$ $\qquad$ (solving for E)

$\approx E^{(0)}_{\mathbf{k}-\mathbf{K}_0} + \sum_{\mathbf{K}\neq\mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} \left|U_{\mathbf{K}-\mathbf{K}_0}\right|^2}{E^{(0)}_{\mathbf{k}-\mathbf{K}_0}-E^{(0)}_{\mathbf{k}-\mathbf{K}}}$ $\qquad$ ($E \approx E^{(0)}_{\mathbf{k}-\mathbf{K}_0}$ in denom)

Conclusion: the NFEM corrections to a nondegenerate free electron level $E^{(0)}_{\mathbf{k}-\mathbf{K}}$ in a weak potential are second-order in the potential's Fourier components.

Weak Potential and Degenerate Solutions

For a fixed wave vector $\mathbf{k}$, consider a set of m reciprocal lattice vectors $\mathbf{K}_1, \ldots, \mathbf{K}_m$ with degenerate free electron energies
$E - E^{(0)}_{\mathbf{k}-\mathbf{K}_i} = 0$ for $i = 1, \ldots, m$

Concept: for a weak potential, the condition that the $E^{(0)}_{\mathbf{k}-\mathbf{K}_i}$ be degenerate generalizes to the near-degeneracy condition
$\left|E^{(0)}_{\mathbf{k}-\mathbf{K}} - E^{(0)}_{\mathbf{k}-\mathbf{K}_i}\right| \gg U_{\mathbf{K}'}$ for all $\mathbf{K} \neq \mathbf{K}_1, \ldots, \mathbf{K}_m$, all $U_{\mathbf{K}'}$, and $i = 1, \ldots, m$.

Interpretation: the free electron energies $E^{(0)}_{\mathbf{k}-\mathbf{K}_i}$ are far from all other free electron energies on the scale of a typical Fourier component $U_{\mathbf{K}'}$.
Goal: analyze how a weak potential perturbs the set of degenerate free electron level with energy $E^{(0)}_{\mathbf{k}-\mathbf{K}_i}$, $i = 1, \ldots, m$.

Approximate Expression for Coefficients

Goal: find approximate expressions for $c_{\mathbf{k}-\mathbf{K}}$ for weak potential and near-degenerate levels $\mathbf{K} = \mathbf{K}_1, \ldots, \mathbf{K}_m$.

$c_{\mathbf{k}-\mathbf{K}'} \sim \begin{cases} \frac{1}{\sqrt{m}} & \mathbf{K}' = \mathbf{K}_1, \ldots, \mathbf{K}_m \\ 0 & \text{otherwise} \end{cases}$ $\qquad$ (near-degenerate level)

$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}}\right) c_{\mathbf{k}-\mathbf{K}} = \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}}$ $\qquad$ (review: NFEM eqs.)

$c_{\mathbf{k}-\mathbf{K}} = \frac{1}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}} \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}}$ $\qquad$ (solved for $c_{\mathbf{k}-\mathbf{K}}$)

$= \frac{1}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}} \left(\sum_{j=1}^{m} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j-\mathbf{K}} \right.$ $\qquad$ (decomposing sum)

$\left. + \sum_{\mathbf{K}'\neq\mathbf{K}_1,\ldots,\mathbf{K}_m} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} \right)$

$\approx \frac{1}{E-E^{(0)}_{\mathbf{k}-\mathbf{K}}} \left(\sum_{j=1}^{m} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j-\mathbf{K}} \right)$ $\qquad$ (using $c_{\mathbf{k}-\mathbf{K}'} \sim 0$)

Solving for Energy

Solve the system of NFEM equations. with the near-degenerate $\mathbf{K} = \mathbf{K}_1, \ldots, \mathbf{K}_m$, giving...
$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_i}\right) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_i}, \ \ i = 1, \ldots, m$

$$= \sum_{j=1}^{m} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j - \mathbf{K}_i} \quad \text{(decomposing sum)}$$
$$+ \sum_{\mathbf{K} \neq \mathbf{K}_1, \ldots, \mathbf{K}_m} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_i}$$

$c_{\mathbf{k}-\mathbf{K}} \approx \frac{1}{E - E^{(0)}_{\mathbf{k}-\mathbf{K}}} \left(\sum_{j=1}^{m} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j - \mathbf{K}} \right)$ (review: near-dg. $c_{\mathbf{k}-\mathbf{K}}$)

Substitute in near-degenerate $c_{\mathbf{k}-\mathbf{K}}$ to get...

$$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_i} \right) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{j=1}^{m} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j - \mathbf{K}_i} + \cdots$$
$$+ \sum_{j=1}^{m} \left(\sum_{\mathbf{K} \neq \mathbf{K}_1, \ldots, \mathbf{K}_m} \frac{U_{\mathbf{K}-\mathbf{K}_i} U_{\mathbf{K}_j - \mathbf{K}}}{E - E^{(0)}_{\mathbf{k}-\mathbf{K}}} \right) c_{\mathbf{k}-\mathbf{K}_j}$$

Conclusion: the NFEM corrections to a set of near-degenerate free electron levels $E^{(0)}_{\mathbf{k}-\mathbf{K}_i}$ in a weak potential are first-order in the potential's Fourier components, and are found by solving a coupled $m \times m$ system of equations.

To leading order in the Fourier components $U_{\mathbf{K}'}$, the near-degenerate equations simplify to...

$$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_i} \right) c_{\mathbf{k}-\mathbf{K}_i} \approx \sum_{j=1}^{m} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j - \mathbf{K}_i} \quad \text{(to leading order)}$$

Example: Twice-Degenerate Level
For a fixed $\mathbf{k}$, consider a set of two reciprocal lattice vectors $\mathbf{K}_1, \mathbf{K}_2$ with near-degenerate energies $E^{(0)}_{\mathbf{k}-\mathbf{K}_i}$ given by...

$\left| E^{(0)}_{\mathbf{k}-\mathbf{K}} - E^{(0)}_{\mathbf{k}-\mathbf{K}_i} \right| \gg U_{\mathbf{K}'}$ for all $\mathbf{K} \neq \mathbf{K}_1, \mathbf{K}_2$, all Fourier components $U_{\mathbf{K}'}$, and for $i = 1, 2$.

Goal: analyze how a weak potential perturbs the two degenerate free electron level with energy $E^{(0)}_{\mathbf{k}-\mathbf{K}_i}$, $i = 1, 2$.

$$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_i} \right) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{j=1}^{2} c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j - \mathbf{K}_i} \quad \text{(for } m = 2\text{)}$$

Use $U_\mathbf{0}$ and write out the two equations to get...

$$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_1} \right) c_{\mathbf{k}-\mathbf{K}_1} = c_{\mathbf{k}-\mathbf{K}_2} U_{\mathbf{K}_2 - \mathbf{K}_1} \quad \text{(for } i = 1\text{)}$$
$$\left(E - E^{(0)}_{\mathbf{k}-\mathbf{K}_2} \right) c_{\mathbf{k}-\mathbf{K}_2} = c_{\mathbf{k}-\mathbf{K}_1} U_{\mathbf{K}_1 - \mathbf{K}_2} \quad \text{(for } i = 2\text{)}$$

Shorthand: let $\mathbf{q} \equiv \mathbf{k} - \mathbf{K}_1$ and $\mathbf{K} \equiv \mathbf{K}_2 - \mathbf{K}_1$

$\mathbf{k} - \mathbf{K}_1 = \mathbf{q} + \mathbf{K}_1 - \mathbf{K}_1 = \mathbf{q}$ (in terms of $\mathbf{q}$ and $\mathbf{K}$)
$\mathbf{k} - \mathbf{K}_2 = \mathbf{q} + \mathbf{K}_1 - \mathbf{K}_2 = \mathbf{q} - \mathbf{K}$ (in terms of $\mathbf{q}$ and $\mathbf{K}$)

$$\left(E^{(0)}_{\mathbf{q}} - E \right) c_{\mathbf{q}} + c_{\mathbf{q}-\mathbf{K}} U_{\mathbf{K}} = 0 \quad \text{(for } i = 1\text{)}$$
$$\left(E^{(0)}_{\mathbf{q}-\mathbf{K}} - E \right) c_{\mathbf{q}-\mathbf{K}} + c_{\mathbf{q}} U_{-\mathbf{K}} = 0 \quad \text{(for } i = 2\text{)}$$
$$\begin{pmatrix} E^{(0)}_{\mathbf{q}} - E & U_{\mathbf{K}} \\ U_{\mathbf{K}}^* & E^{(0)}_{\mathbf{q}-\mathbf{K}} - E \end{pmatrix} \begin{pmatrix} c_{\mathbf{q}} \\ c_{\mathbf{q}-\mathbf{K}} \end{pmatrix} = \mathbf{0} \quad \text{(in matrix form)}$$

For a non-trivial solution for $c_{\mathbf{q}}$ and $c_{\mathbf{q}-\mathbf{K}}$, we require...

$$\det \begin{pmatrix} E^{(0)}_{\mathbf{q}} - E & U_{\mathbf{K}} \\ U_{\mathbf{K}}^* & E^{(0)}_{\mathbf{q}-\mathbf{K}} - E \end{pmatrix} = 0$$
$$\implies E = \frac{1}{2} \left(E^{(0)}_{\mathbf{q}} + E^{(0)}_{\mathbf{q}-\mathbf{K}} \right) \pm \frac{1}{2} \sqrt{\left(E^{(0)}_{\mathbf{q}} - E^{(0)}_{\mathbf{q}-\mathbf{K}} \right)^2 + 4|U_{\mathbf{K}}|^2}$$

Interpretation: $\frac{1}{2} \left(E^{(0)}_{\mathbf{q}} + E^{(0)}_{\mathbf{q}-\mathbf{K}} \right) = \frac{1}{2} \left(E^{(0)}_{\mathbf{k}-\mathbf{K}_1} + E^{(0)}_{\mathbf{k}-\mathbf{K}_2} \right)$ is degenerate free electron energy. The square root term breaks the degeneracy assuming non-zero $U_{\mathbf{K}} = U_{\mathbf{K}_2 - \mathbf{K}_1}$.

Bragg Plane Interpretation of Double Degeneracy
Double near-degeneracy condition: $E^{(0)}_{\mathbf{q}-\mathbf{K}} \approx E^{(0)}_{\mathbf{q}}$ and $\left| E^{(0)}_{\mathbf{q}} - E^{(0)}_{\mathbf{q}-\mathbf{K}'} \right| \gg U_{\mathbf{K}''}$ for all $\mathbf{K}' \neq \mathbf{K}$ and all $U_{\mathbf{K}''}$.

Concept: $E^{(0)}_{\mathbf{q}-\mathbf{K}} = E^{(0)}_{\mathbf{q}}$ only for reciprocal lattice vectors $\mathbf{K}$ for which $|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$.

$|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$ (for double degeneracy)
$|\mathbf{q}|^2 = |\mathbf{q} - \mathbf{K}|^2$ (squaring)
$q^2 = q^2 - 2\mathbf{q} \cdot \mathbf{K} - K^2$ (multiplying out)
$\mathbf{q} \cdot \mathbf{K} = \frac{K^2}{2}$ (simplified and rearranged)
$\mathbf{q} \cdot \hat{\mathbf{K}} = \frac{K}{2}$ (letting $\hat{\mathbf{K}} \equiv \mathbf{K}/|\mathbf{K}|$)

Interpretation: $\mathbf{q} \cdot \hat{\mathbf{K}} = K/2$ is the equation of Bragg plane

defined by the reciprocal lattice vector $\mathbf{K} \implies$ the degeneracy condition $E^{(0)}_{\mathbf{q}} = E^{(0)}_{\mathbf{q}-\mathbf{K}}$ is satisfied for $\mathbf{q}$ falling in the Bragg plane defined by $\mathbf{K}$.

Energy Gradient
Goal: evaluate the gradient of the electron energy at a doubly-degenerate level $E^{(0)}_{\mathbf{q}} = E^{(0)}_{\mathbf{q}-\mathbf{K}}$ in a weak potential.

$E_{\mathbf{q}} = \frac{1}{2} \left(E^{(0)}_{\mathbf{q}} + E^{(0)}_{\mathbf{q}-\mathbf{K}} \right)$ (review: doubly-degenerate level)
$\pm \frac{1}{2} \sqrt{\left(E^{(0)}_{\mathbf{q}} - E^{(0)}_{\mathbf{q}-\mathbf{K}} \right)^2 + 4|U_{\mathbf{K}}|^2}$

$\nabla_{\mathbf{q}} E_{\mathbf{q}} \big|_{E^{(0)}_{\mathbf{q}} = E^{(0)}_{\mathbf{q}-\mathbf{K}}} = \frac{1}{2} \nabla_{\mathbf{q}} \left(E^{(0)}_{\mathbf{q}} + E^{(0)}_{\mathbf{q}-\mathbf{K}} \right)_{E^{(0)}_{\mathbf{q}} = E^{(0)}_{\mathbf{q}-\mathbf{K}}} + \mathbf{0}$

(square root term vanishes when evaluated at $E^{(0)}_{\mathbf{q}} = E^{(0)}_{\mathbf{q}-\mathbf{K}}$)

$\nabla_{\mathbf{q}} E_{\mathbf{q}} = \frac{\hbar^2}{4m} \nabla_{\mathbf{q}} \left(|\mathbf{q}|^2 + |\mathbf{q} - \mathbf{K}|^2 \right)$ (at $E^{(0)}_{\mathbf{q}} = E^{(0)}_{\mathbf{q}-\mathbf{K}}$)
$= \frac{1}{2} \frac{\hbar^2}{2m} \nabla_{\mathbf{q}} \left(2|\mathbf{q}|^2 - 2\mathbf{q} \cdot \mathbf{K} + |\mathbf{K}|^2 \right)$ (multiplying out)
$= \frac{\hbar^2}{4m} (4\mathbf{q} - 2\mathbf{K} + \mathbf{0})$ (evaluating gradient)
$= \frac{\hbar^2}{m} \left(\mathbf{q} - \frac{\mathbf{K}}{2} \right)$ (simplifying)

Conclusion: $\nabla_{\mathbf{q}} E_{\mathbf{q}}$ lies in the Bragg plane defined by the RL vector $\mathbf{K}$. Meanwhile, by definition, $\nabla_{\mathbf{q}} E_{\mathbf{q}}$ points in the direction of greatest change in $E_{\mathbf{q}}$ with respect to $\mathbf{q}$, and thus perpendicular to planes of constant $E_{\mathbf{q}} \implies$ planes of constant $E_{\mathbf{q}}$ are perpendicular to the Bragg plane defined by $\mathbf{K}$.

The Tight-Binding Model
Model: Assume e^- are tightly bound to lattice sites and interact appreciably only with nearby lattice sites; expand Bloch e^- eigenstates over a basis of hydrogen-like atomic eigenfunctions. The TBM applies to insulators and to energy bands associated with partially-filled d shells in transition metals.

Review: Isolated Single-Electron Atom
Consider a single-electron (mass m) in the presence of a proton (mass $M \gg m$), isolated from external interactions.
Align origin of coordinate system with proton's center.
$U_{\text{at}} = -\frac{e_0^2}{4\pi\epsilon_0 r}$ (the atomic sytem's Coulomb potential)
$\mu = \frac{mM}{m+M} \approx m$ (reduced mass)
$H_{\text{at}} = -\frac{\hbar^2}{2\mu} \nabla^2 - U_{\text{at}}$ (system's Hamiltonian)
$\approx -\frac{\hbar^2}{2m} \nabla^2 - \frac{e_0^2}{4\pi\epsilon r}$ (since $\mu \approx m$)
$H_{\text{at}} \psi_{nlm_l} = E_{nlm_l} \psi_{nlm_l}$ (electron Schrödinger equation)
ψ_{nlm_l} are electron energy eigenfunctions
n is principal quantum number
l is orbital quantum number
m_l is magnetic quantum number
Let $\nu \equiv (n, l, m_l)$ (tuple quantum number, for shorthand)
$H_{\text{at}} \psi_\nu = E_\nu \psi_\nu$ (e^- Schrödinger eq. in terms of ν)

Single-Electron Atom in Periodic Potential
Consider a single-electron atom at the origin of a surrounding crystal lattice of identical atoms.
Motivation: the TBM assumes that near lattice sites the lattice Hamiltonian is well-approximated by an atomic Hamiltonian.
$U_{\text{at}}(\mathbf{r}) = -\frac{e_0^2}{4\pi\epsilon_0 r}$ (a single atom's potential)
$U_{\text{lattice}}(\mathbf{r}) = \sum_{\mathbf{R}} U_{\text{at}}(\mathbf{r} - \mathbf{R})$ (the lattice's potential)
$\Delta U \equiv \sum_{\mathbf{R} \neq \mathbf{0}} U_{\text{at}}(\mathbf{r} - \mathbf{R})$ (lattice potential minus origin atom)
$H_{\text{at}} = -\frac{\hbar^2}{2m} \nabla^2 + U_{\text{at}}(\mathbf{r})$ (for isolated atom at origin)
$H = H_{\text{at}} + \Delta U,$ (for atom at orign plus lattice)
$\approx H_{\text{at}}$ (near origin atom)

TBM Ansatz for Bloch Electrons
Let $\nu = (n, l, m_l)$ be a shorthand tuple index of quantum numbers for isolated atomic eigenfunctions.
ψ_ν are isolated atomic eigenfunctions.

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\phi(\mathbf{r}-\mathbf{R}) \qquad \text{(TBM ansatz for Bloch } e^-)$$
$$\phi(\mathbf{r}) = \sum_{\nu} b_\nu \psi_\nu(\mathbf{r}) \qquad \text{(TBM basis function)}$$

Interpretation: $\phi(\mathbf{r})$ is a linear combination of (in practice, a small number of) atomic eigenfunctions.

TBM: Solving the Schrödinger Equation I

Goal: Solve the Schrödinger equation for electrons in a periodic potential using the TBM ansatz $\psi(\mathbf{r})$.

$$\left(H_{\text{at}} + \Delta U\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad \text{(review: Schrödinger equation)}$$

Take scalar product with arbitrary atomic eigenfun. ψ_μ to get...

$$\iiint \psi_\mu^*(H_{\text{at}} + \Delta U)\psi\, dV = E\iiint \psi_\mu^*\psi\, dV$$
$$\iiint \psi_\mu^* H_{\text{at}}\psi\, dV = E_\mu \iiint \psi_\mu^*\psi\, dV \qquad \text{(using } H_{\text{at}}\psi_\mu^* = E_\mu\psi_\mu^*)$$

Substitute TBM ansatz for ψ into scalar product to get...

$$\iiint \psi_\mu^*\psi\, dV = \iiint \psi_\mu^* \sum_{\nu,\mathbf{R}} e^{ik\mathbf{R}}b_\nu\psi_\nu(\mathbf{r}-\mathbf{R})\, dV$$
$$= \sum_{\nu,\mathbf{R}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV$$

$$\iiint \psi_\mu^*\psi_\nu(\mathbf{r})\, dV = \delta_{\nu,\mu} \qquad \text{(if } \mathbf{R}=\mathbf{0}, \text{ since } \psi_\nu \text{ are orthonormal)}$$

Decompose sum over $\mathbf{R}$ into $\mathbf{R}=\mathbf{0}$ and $\mathbf{R}\neq\mathbf{0}$ to get...

$$\iiint \psi_\mu^*\psi\, dV = b_\nu\delta_{\nu,\mu} + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV$$
$$= b_\mu + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV$$

Summarizing Results So Far

$$\iiint \psi_\mu^* H\psi\, dV = E_\mu \iiint \psi_\mu^*\psi\, dV \qquad (i)$$
$$\iiint \psi_\mu^*\psi\, dV = b_\mu + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV \qquad (ii)$$

TBM: Solving the Schrödinger Equation II

Continue with scalar product of Schrödinger eq. with ψ_μ^*, i.e.

$$\iiint \psi_\mu^*(H_{\text{at}} + \Delta U)\psi\, dV = E\iiint \psi_\mu^*\psi\, dV$$
$$E\iiint \psi_\mu^*\psi\, dV - \iiint \psi_\mu^* H_{\text{at}}\psi\, dV = \iiint \psi_\mu^*\Delta U\psi\, dV \quad \text{(rearranged)}$$

Substitute in results from Part I to get..

$$(E - E_\mu)\iiint \psi_\mu^*\psi\, dV = \iiint \psi_\mu^*\Delta U\psi\, dV \qquad \text{(using result (i))}$$
$$(E-E_\mu)\left[b_\mu + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV\right] = \iiint \psi_\mu^*\Delta U\psi\, dV$$

(using result (ii))

Finally, substitute ansatz for ψ into RHS, rearrange integration and summation, and decompose sum over $\mathbf{R}$ into $\mathbf{R}=\mathbf{0}$ and $\mathbf{R}\neq\mathbf{0}$ to get...

$$(E - E_\mu)\left[b_\mu + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV\right] = \cdots$$
$$\cdots = \sum_\nu b_\nu \iiint \psi_\mu^*\Delta U(\mathbf{r})\psi_\nu(\mathbf{r})\, dV + \cdots$$
$$\cdots + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*(\mathbf{r})\Delta U(\mathbf{r})\psi_\nu(\mathbf{r}-\mathbf{R})\, dV$$

Interpretation: in principle, this result is a system of equations for the coefficients b_ν used in the TBM ansatz for electron wave functions $\psi(\mathbf{r})$.

Simplifications

Concept: in the tight-binding approximation of highly-localized electron levels, overlap integrals are small.

$$\iiint \psi_\mu^*(\mathbf{r})\psi_\nu(\mathbf{r}-\mathbf{R})\, dV \approx 0 \qquad \text{(overlap integrals are small)}$$
$$\iiint \psi_\mu^*(\mathbf{r})\Delta U\psi_\nu(\mathbf{r}-\mathbf{R})\, dV \approx 0 \qquad \text{(overlap integrals are small)}$$

Concept: atomic wave functions $\psi_n(\mathbf{r})$ are small at wherever lattice Hamiltonian differs appreciably from atomic Hamiltonian, i.e. wherever $\Delta U(\mathbf{r})$ is large.

$$\iiint \psi_\mu^*(\mathbf{r})\Delta U\psi_\nu(\mathbf{r})\, dV \approx 0 \qquad \text{(assuming } \psi_n\Delta U \text{ is small)}$$

Use the above simplifications to make the approximation...

$$(E - E_\mu)b_\mu \approx 0 \qquad \text{(approximate TBM result)}$$

Interpretation: the TBM predicts that the Bloch electron energy E must be close to some atomic energy E_0, implying...
$E \approx E_0$ and $b_\mu \approx 0$ if $E_\mu \not\approx E_0$

Example: Tight-Binding Model and the s Orbital

Consider only electrons in s orbital where $(l = 0, m_l = 0)$

$$b_\nu \approx \begin{cases} b_s & \nu \text{ is an } s \text{ orbital} \\ 0 & \text{otherwise} \end{cases} \qquad \text{(consider only } s \text{ orbital)}$$
$$\sum_\nu b_\nu \approx b_s \qquad \text{(neglecting other orbitals)}$$
$$(E - E_\mu)\left[b_\mu + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*\psi_\nu(\mathbf{r}-\mathbf{R})\, dV\right] = \cdots$$
$$\cdots = \sum_\nu b_\nu \iiint \psi_\mu^*\Delta U(\mathbf{r})\psi_\nu(\mathbf{r})\, dV + \cdots \qquad \text{(general TBM eqs.)}$$
$$\cdots + \sum_{\nu,\mathbf{R}\neq\mathbf{0}} b_\nu e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_\mu^*(\mathbf{r})\Delta U(\mathbf{r})\psi_\nu(\mathbf{r}-\mathbf{R})\, dV$$

Considering only the s orbital, this simplifies to...

$$(E - E_s)\left[b_s + \sum_{\mathbf{R}\neq\mathbf{0}} b_s e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_s^*\psi_s(\mathbf{r}-\mathbf{R})\, dV\right]$$
$$\cdots = b_s \iiint \psi_s^*\Delta U(\mathbf{r})\psi_s(\mathbf{r})\, dV + \cdots \qquad \text{(for } s \text{ orbital only)}$$
$$\cdots + \sum_{\mathbf{R}\neq\mathbf{0}} b_s e^{i\mathbf{k}\cdot\mathbf{R}} \iiint \psi_s^*(\mathbf{r})\Delta U(\mathbf{r})\psi_s(\mathbf{r}-\mathbf{R})\, dV$$

For shorthand, define the following overlap integrals...

$$\alpha(\mathbf{R}) \equiv \iiint \psi_s^*\psi_s(\mathbf{r}-\mathbf{R})\, dV$$
$$\beta \equiv -\iiint \psi_s^*\Delta U(\mathbf{r})\psi_s(\mathbf{r})\, dV$$
$$\gamma(\mathbf{R}) \equiv -\iiint \psi_s^*(\mathbf{r})\Delta U(\mathbf{r})\psi_s(\mathbf{r}-\mathbf{R})\, dV$$

In terms of α, β, γ, the system of eqs. for E becomes...

$$(E - E_s)b_s + (E - E_s)\sum_{\mathbf{R}\neq\mathbf{0}} b_s e^{i\mathbf{k}\cdot\mathbf{R}}\alpha(\mathbf{R}) = -b_s\beta - \sum_{\mathbf{R}\neq\mathbf{0}} b_s e^{i\mathbf{k}\cdot\mathbf{R}}\gamma(\mathbf{R})$$

Cancel b_s to get...

$$E - E_s + (E - E_s)\sum_{\mathbf{R}\neq\mathbf{0}} e^{i\mathbf{k}\cdot\mathbf{R}}\alpha(\mathbf{R}) = -\beta - \sum_{\mathbf{R}\neq\mathbf{0}} e^{i\mathbf{k}\cdot\mathbf{R}}\gamma(\mathbf{R})$$

Solve for TBM electron energy $E = E(\mathbf{k})$ to get...

$$E(\mathbf{k}) = E_s - \frac{\beta + \sum_{\mathbf{R}\neq\mathbf{0}} \gamma(\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}}{1 + \sum_{\mathbf{R}\neq\mathbf{0}} \alpha(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{R}}} \qquad \textbf{(TBM for } s \textbf{ orbital)}$$

In Practice:

- Neglect $\alpha(\mathbf{R})$ (because TBM overlap integrals are small)

- Sum only over nearest neighbor $\mathbf{R}$

$$E(\mathbf{k}) = E_s - \beta - \sum_{\mathbf{R}\in\{\text{nn}\}} \gamma(\mathbf{R})\cos(\mathbf{k}\cdot\mathbf{R}) \qquad \text{(with above approxs.)}$$

Semiclassical Electron Dynamics

Goal: provide a semi-classical formalism for analyzing electron dynamics in a periodic potential.

Summary of Free Electron Dynamics

Consider a free electron with wave vector $\mathbf{k}$

$$\psi_\mathbf{k}(\mathbf{r}) \propto e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \text{(free electron wave function)}$$
$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \qquad \text{(free electron energy)}$$
$$\mathbf{p} = \hbar\mathbf{k} \qquad \text{(free electron momentum)}$$
$$\mathbf{v} = \frac{\hbar\mathbf{k}}{m} = \frac{1}{\hbar}\nabla_\mathbf{k} E(\mathbf{k}) \qquad \text{(free electron velocity)}$$

Free electron wave functions are eigenfunctions of the quantum-mechanical momentum operator with eigenvalue $\hbar\mathbf{k}$!

$$\hat{\mathbf{p}}\psi_\mathbf{k} = -i\hbar\nabla A e^{i\mathbf{k}\cdot\mathbf{r}} = -i^2\hbar\mathbf{k}A e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}\psi_\mathbf{k} \quad \text{(eigval. relation)}$$

Summary: Electrons in a Periodic Potential

Electrons in a periodic potential are called *Bloch electrons*

A Bloch electron's state is determined by its wave vector $\mathbf{k}$ and band index n

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \qquad \text{(Bloch electron wave function)}$$

$u_{n\mathbf{k}}$ is a periodic function with period of the underlying Bravais lattice Λ, i.e. $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ for all $\mathbf{R}\in\Lambda$.

The Bloch Equations

The Bloch equations govern the dynamics of electrons in a periodic potential under the influence of an external electric field $\mathcal{E}$ and magnetic field $\mathbf{B}$

Assumptions

(i) Electron energy band index n is conserved (electrons cannot jump between energy bands).

(ii) A Bloch electron's wave vector is undetermined up to an arbitrary reciprocal lattice vector $\mathbf{K}$, i.e. $\mathbf{k}$ and $\mathbf{k}+\mathbf{K}$

describe equivalent levels.

(iii) The velocity of a Bloch electron is...
$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k})$ **(velocity of Bloch electron)**

(iv) The dynamics of a Bloch electron are governed by...
$\hbar\frac{d\mathbf{k}}{dt} = -e_0[\boldsymbol{\mathcal{E}} + \mathbf{v}_n \times \mathbf{B}]$ **(Bloch electron dynamics)**

Electron Dynamics: Informal Derivation

Consider an electron in the n-th energy band in an external electric field $\boldsymbol{\mathcal{E}}$ with electric potential $\phi = \phi(\mathbf{r},t)$

$E_{\text{tot}} = E_n(\mathbf{k}) - e_0\phi(\mathbf{r},t)$ (total electron energy)

$E_{\text{tot}} = \text{constant}$ (total e^- energy is a constant of motion)

$\dot{E}_{\text{tot}} = \frac{d\mathbf{k}}{dt}\nabla_{\mathbf{k}}E_n(\mathbf{k}) - e_0\frac{d\mathbf{r}}{dt}\nabla_{\mathbf{r}}\phi(\mathbf{r},t)$ (chain rule)

$= \left(\hbar\frac{d\mathbf{k}}{dt}\right)\frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k}) + e_0\frac{d\mathbf{r}}{dt}\boldsymbol{\mathcal{E}}$ $(\boldsymbol{\mathcal{E}} = -\nabla_{\mathbf{r}}\phi)$

$= \hbar\frac{d\mathbf{k}}{dt}\mathbf{v}_n(\mathbf{k}) + e_0\frac{d\mathbf{r}}{dt}\boldsymbol{\mathcal{E}}$ (recognizing $\mathbf{v}_n(\mathbf{k})$)

$= \hbar\frac{d\mathbf{k}}{dt}\mathbf{v}_n(\mathbf{k}) + e_0\mathbf{v}_n(\mathbf{k})\boldsymbol{\mathcal{E}}$ (assuming $\mathbf{v}_n(\mathbf{k}) = \frac{d\mathbf{r}}{dt}$)

$= \mathbf{v}_n(\mathbf{k}) \cdot \left[\hbar\frac{d\mathbf{k}}{dt} + e_0\boldsymbol{\mathcal{E}}\right] = 0$ (factoring)

Idea: the dot product equality $\mathbf{v} \cdot \left[\hbar\frac{d\mathbf{k}}{dt} + e_0\boldsymbol{\mathcal{E}}\right] = 0$ still holds if we include terms *orthogonal* to $\mathbf{v}$ in the brackets. We thus add on $\mathbf{v} \times \mathbf{B}$ to get...

$\mathbf{v}_n(\mathbf{k}) \cdot \left[\hbar\frac{d\mathbf{k}}{dt} + e_0\boldsymbol{\mathcal{E}} + \mathbf{v} \times \mathbf{B}\right] = 0$ (adding on $\mathbf{v} \times \mathbf{B}$)

$\implies \hbar\frac{d\mathbf{k}}{dt} + e_0\boldsymbol{\mathcal{E}} + \mathbf{v}_n \times \mathbf{B} = \mathbf{0}$ (second Bloch equation)

Bloch Electron in a Magnetic Field

Consider Bloch electron in a homogeneous magnetic field

$\mathbf{B}(\mathbf{r},t) = B_0\,\hat{\mathbf{e}}_z$ with B_0 constant (homog. magnetic field)

$\mathbf{v}_n = \frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k})$ (review: Bloch e_- velocity)

$\hbar\frac{d\mathbf{k}}{dt} = -e_0(\boldsymbol{\mathcal{E}} + \mathbf{v}_n \times \mathbf{B})$ (review: Bloch e_- dynamics)

$= -e_0\mathbf{v}_n \times \mathbf{B}$ (assume zero external $\boldsymbol{\mathcal{E}}$ field)

$\left[\mathbf{v}_n(\mathbf{k}) \times \mathbf{B}\right]_z = 0 \implies \frac{dk_z}{dt} = 0$ (for $\mathbf{B} = B_0\,\hat{\mathbf{e}}_z$)

$\implies k_z$ is a constant of motion in a homog. magnetic field

$\frac{d}{dt}E_n(\mathbf{k}) = \frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}}E_n(\mathbf{k})$ (chain rule)

$= \frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k}) \cdot \left(\hbar\frac{d\mathbf{k}}{dt}\right)$ (multiply/divide by $\hbar$)

$= -\mathbf{v}_n(\mathbf{k}) \cdot (e_0\mathbf{v}_n \times \mathbf{B})$ (Bloch equations)

$= 0$ (since $\mathbf{v}_n \perp (\mathbf{v}_n \times \mathbf{B})$ by construction)

Conclusion: in a homogeneous magnetic field $\mathbf{B} = B_0\,\hat{\mathbf{e}}_z$...

(i) k_z is a constant of motion

(ii) $E_n(\mathbf{k})$ is a constant of motion.

Physical interpretation: E_n is constant because a magnetic field cannot do work.

Bloch Oscillations

Consider an electron in a constant, homogeneous electric field $\boldsymbol{\mathcal{E}}(\mathbf{r},t) = \boldsymbol{\mathcal{E}}_0$ and no external magnetic field.

$\hbar\frac{d\mathbf{k}}{dt} = -e_0\left[\boldsymbol{\mathcal{E}} + \mathbf{v}_n(\mathbf{k}) \times \mathbf{B}\right]$ (Bloch electron dynamics)

$= -e_0\boldsymbol{\mathcal{E}}_0$ (in homogeneous electric field)

$\mathbf{k}(t) = \mathbf{k}_0 - \frac{e_0\boldsymbol{\mathcal{E}}_0}{\hbar}t$ (solved for $\mathbf{k}(t)$)

Conclusion: an electron's wave vector $\mathbf{k}$ increases linearly with time in a homogeneous external field.

Complication: as $\mathbf{k}$ increases, $E_n(\mathbf{k})$ also increases, and eventually $E_n(\mathbf{k})$ would reach end of energy band.

Resolution: in a periodic potential, $E_n(\mathbf{k})$ is a periodic function of $\mathbf{k}$, so $E_n(\mathbf{k})$ is bounded above and below and energy band index is fixed.

Example: Bloch Oscillations in One Dimension

Consider an electron in a one-dimensional Bravais lattice with lattice constant a and known TBM overlap integral γ.

$k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ (first Brillioun zone)

Using the tight-binding model, the electron's energy is...

$E(k) = -\gamma\cos(ka)$ (see "**TBM and the s Orbital**")

$\mathbf{k}(t) = \mathbf{k}_0 - \frac{e_0\boldsymbol{\mathcal{E}}_0}{\hbar}t$ (in three dimensions)

$k(t) = -\frac{e_0\mathcal{E}}{\hbar}t$ (in one dimension, neglecting k_0)

$\implies E(k(t)) = -\gamma\cos\left(\frac{e_0\mathcal{E}a}{\hbar}t\right)$ (using above $k(t)$)

Conclusion: although k increases linearly with time in an external electric field, electron energy *oscillates* because of the electron's sinusoidal energy dispersion relation. The electron energy's oscillation with time are called *Bloch oscillations*.

Analyzing One-Dimensional Bloch Oscillations

$E(k(t)) = -\gamma\cos\left(\frac{e_0\mathcal{E}a}{\hbar}t\right)$ (Bloch oscillations)

Consider one period t_{B} of a Bloch oscillation...

$\frac{ae_0\mathcal{E}}{\hbar}t_{\text{B}} = 2\pi$ (eq. for Bloch oscillation period t_{B})

$\implies t_{\text{B}} = \frac{2\pi\hbar}{e_0 a\mathcal{E}}$ (solving for t_{B})

$v(k) = \frac{1}{\hbar}\frac{d}{dk}E_n(k) = -\frac{\gamma}{\hbar}\frac{d}{dk}\cos(ka)$ (e^- velocity in 1D)

$= \frac{\gamma a}{\hbar}\sin(ka)$ (differentiating)

$v(k(t)) = -\frac{\gamma a}{\hbar}\sin\left(\frac{e_0\mathcal{E}}{\hbar}t\right)$ (using $k(t) = -\frac{e_0\mathcal{E}}{\hbar}t$)

$x(k(t)) = \int v(t)\,dt = \frac{\gamma}{e_0\mathcal{E}}\cos\left(\frac{e_0 a\mathcal{E}}{\hbar}t\right) + x_0$ (e^- position)

$x_{\text{B}} = \frac{\gamma}{e_0\mathcal{E}}$ (1D Bloch oscillation amplitude)

In Passing: Validity of Semiclassical Equations

Consider electrons in the n-th band of a material with Fermi energy E_{F} and band gap E_{gap} between the n-th band and closest band with $n' \neq n$.

The semiclassical analysis neglects the possibility that electrons jump between energy bands. Without proof, this assumption is valid in the regime...

$ae_0\mathcal{E} \ll \frac{E_{\text{gap}}^2}{E_{\text{F}}}$ (condition for constant band index)

$\hbar\frac{e_0 B}{m} \ll \frac{E_{\text{gap}}^2}{E_{\text{F}}}$ (condition for constant band index)

For orientation, typical parameter values might be $a \sim 0.1\,\text{nm}$ and $\mathcal{E} \sim 10^{-2}\,\text{V cm}^{-1} \implies ae_0\mathcal{E} \sim 10^{-10}\,\text{eV}$.

$E_{\text{F}} \sim 1\,\text{eV}$ to $10\,\text{eV}$ in metals

$E_{\text{gap}} \sim 1\,\text{eV}$ in metals

$\implies ae_0\mathcal{E} \sim 10^{-10}\,\text{eV} \ll \frac{E_{\text{gap}}^2}{E_{\text{F}}} \sim 0.1\,\text{eV}$

Conclusion: condition for constant band index is often satisfied in practice.

Energy Band Occupation and Conduction

Condition for Filled Bands

In a ground state, a filled energy band is a band in which all energies $E_n(\mathbf{k})$ are below the crystal's Fermi energy E_{F}.

Generally, a filled band is one in which $\mu(T) - E_n(\mathbf{k}) \gg k_{\text{B}}T$, so that $f(E_n(\mathbf{k})) \approx 1$ for all $\mathbf{k}$ in the band.

$E_n(\mathbf{k}) < E_{\text{F}}$ for all $\mathbf{k}$ (filled n-th band, ground state)

$\mu - E_n(\mathbf{k}) \gg k_{\text{B}}T$ for all $\mathbf{k}$ (filled n-th band, finite temp.)

$n_{\mathbf{k}} = \frac{d^3\mathbf{k}}{4\pi^3}$ (review: density of allowed $\mathbf{k}$ in region $d^3\mathbf{k}$)

Review: band index n is preserved in the semiclassical model

Consequence: since band index is conserved, a filled band will remain filled for all time, neglecting inter-band transitions.

Electron Current in Filled Bands

Goal: generalize the free electron expression $\mathbf{j}_{\text{el}} = -n_e e_0\mathbf{v}$ to Bloch electrons in a filled energy band.

$n_{\mathbf{k}} = \frac{d^3\mathbf{k}}{4\pi^3}$ (review: density of allowed $\mathbf{k}$)

$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k})$ (review: Bloch electron velocity)

Concept: in a filled energy band, integrating over the first BZ will account for all electron levels in the band.

$\mathbf{j}_{\text{el}}^{(n)} = -e_0\iiint_{\text{BZ}}\mathbf{v}_n(\mathbf{k})\frac{d^3\mathbf{k}}{4\pi^3}$ (current density in filled band)

$= -\frac{e_0}{\hbar}\iiint_{\text{BZ}}\nabla_{\mathbf{k}}E_n(\mathbf{k})\frac{d^3\mathbf{k}}{4\pi^3}$ (in terms of $E_n(\mathbf{k})$)

Heat Current in Filled Bands

Goal: generalize the free electron expression $\mathbf{j}_{\text{el}} = n_e E\mathbf{v}$ to Bloch electrons in a filled energy band.

$n_{\mathbf{k}} = \frac{d^3\mathbf{k}}{4\pi^3}$ (review: density of allowed $\mathbf{k}$)

$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k})$ (review: Bloch electron velocity)

Concept: in a filled energy band, integrating over the first BZ will account for all electron levels in the band.

$\mathbf{j}_{\text{heat}}^{(n)} = \iiint E_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\frac{d^3\mathbf{k}}{4\pi^3}$ (heat current in filled band)

$$= \frac{1}{\hbar} \iiint E_n(\mathbf{k}) \nabla_{\mathbf{k}} E_n(\mathbf{k}) \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} \qquad \text{(in terms of } E_n(\mathbf{k}))$$
$$= \frac{1}{2\hbar} \iiint \nabla_{\mathbf{k}} \left[E_n(\mathbf{k})^2 \right] \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} \qquad \text{(reverse-engineered gradient)}$$

Full Bands Cannot Carry Current

Fully-occupied electron energy bands do not carry either electric current or heat current.

Justification: both $E_n(\mathbf{k})$ and $\left[E_n(\mathbf{k}) \right]^2$ are periodic over the first Brillioun zone. The integral of a periodic function over one period is zero, so the integrals in both $\mathbf{j}_n^{(\mathrm{el})}$ and $\mathbf{j}_n^{(\mathrm{E})}$ are zero.

Condition the a Material Be an Insulator

Underlying concept:

- Fully-occupied electron energy bands do not carry either electric current or heat current.

- Consequence: only partially-filled bands should be considered in determined a solid's insulating properties.

$\implies$ Materials with *only* filled ground-state bands are insulators.

$\implies$ Materials with some partially-filled ground-state bands are conductors.

Consider a crystal with N lattice sites, resulting in N possible values of $\mathbf{k}$ in the crystal's first Brillioun zone.

- Each $\mathbf{k}$ level can be occupied by two e^- (spin up/spin down).

- Each energy band can thus hold $2N$ electron levels.

- Solids with only filled bands are insulators.

Combine the above three ideas to conclude... *A necessary condition for a material to have only filled bands is that the material have an even number of valence electrons.*

Holes

$$\mathbf{j}_e = -e_0 \iiint_{\mathrm{occupied}} \mathbf{v}(\mathbf{k}) \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} \qquad \text{(general electron current)}$$

Review: filled bands cannot carry current.

$$\mathbf{j}_{\mathrm{full}} = -e_0 \iiint_{\mathrm{BZ}} \mathbf{v}(\mathbf{k}) \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} = \mathbf{0} \qquad \text{(in a filled band)}$$

Idea: decompose integral over entire BZ in a full band into integrals over the occupied and empty levels.

$$\mathbf{j}_{\mathrm{full}} = -e_0 \iiint_{\mathrm{BZ}} \mathbf{v} \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} = \mathbf{0}$$
$$= -e_0 \iiint_{\mathrm{occupied}} \mathbf{v} \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} + (-e_0) \iiint_{\mathrm{empty}} \mathbf{v} \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} = \mathbf{0}$$
$$\implies (-e_0) \iiint_{\mathrm{occupied}} \mathbf{v} \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3} = (+e_0) \iiint_{\mathrm{empty}} \mathbf{v} \frac{\mathrm{d}^3 \mathbf{k}}{4\pi^3}$$

Conclusion: current $\mathbf{j}_e$ due to electrons in all occupied levels is identical to the current due to fictitious particles of positive charge, called *holes*, in all empty levels.

The Effective Mass Tensor

Goal: develop a method allowing the use of *free* electron expressions (Fermi function, density of levels, etc...) to approximately describe the dynamics of *Bloch* electrons.

Rough summary of results: replacing free electron mass m with an effective mass tensor m permits the use of free electron expressions for Bloch electrons.

Expansion of Bloch Electron Dispersion

Consider an electron energy band with known dispersion relation $E_n(\mathbf{k})$ and a parabolic minimum centered at $\mathbf{k} = \mathbf{k}_0$.

Let $\delta \mathbf{k} = \mathbf{k} - \mathbf{k}_0$ (position from minimum point)

Expand the dispersion relation to second order in $\mathbf{k}$ about the minimum point $\mathbf{k}_0$ (using summation convention) to get...

$$E_n(\mathbf{k}) \approx E_n(\mathbf{k}_0) + \frac{\partial E_n(\mathbf{k})}{\partial k_i}\Big|_{\mathbf{k}_0} \delta k_i + \frac{1}{2} \frac{\partial^2 E_n(\mathbf{k})}{\partial k_i \partial k_j}\Big|_{\mathbf{k}_0} \delta k_i \delta k_j$$
$$= E_n(\mathbf{k}_0) + \frac{1}{2} \frac{\partial^2 E_n(\mathbf{k})}{\partial k_i \partial k_j}\Big|_{\mathbf{k}_0} \delta k_i \delta k_j \quad \text{(first derivatives of } E_n$$
must vanish at the minimum $\mathbf{k}_0$)

Review: Free Electron Dispersion

$$E_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \qquad \text{(free electron dispersion)}$$
$$\implies \frac{2E_0}{\hbar^2 k^2} = \frac{1}{m} = \frac{1}{\hbar^2} \frac{\partial^2 E_0}{\partial k^2}$$
$$\implies m^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \qquad \text{(for free electrons)}$$
$$E_0(\mathbf{k}) = \frac{1}{2\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \cdot (\hbar^2 k^2) \qquad \text{(in terms of above } 1/m)$$

Introducing the Effective Mass Tensor

$$E_n(\mathbf{k}) \approx E_n(\mathbf{k}_0) + \frac{1}{2} \frac{\partial^2 E_n}{\partial k_i \partial k_j}\Big|_{\mathbf{k}_0} \delta k_i \delta k_j \qquad \text{(Bloch electrons)}$$
$$E_0(\mathbf{k}) = \frac{1}{2\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \cdot (\hbar^2 k^2) \qquad \text{(free electrons)}$$
$$m^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \qquad \text{(free electrons)}$$

Comparing expressions for free and Bloch electrons motivates the definition of an effective mass tensor m according to...

$$\left[\mathsf{m}_n^{-1}(\mathbf{k}) \right]_{ij} = \pm \frac{1}{\hbar^2} \frac{\partial^2 E_n(\mathbf{k})}{\partial k_i \partial k_j} \qquad \textbf{(effective mass tensor)}$$

Plus sign corresponds to effective mass of electrons.
Minus sign corresponds to effective mass of holes.

$$E_n(\mathbf{k}_0 + \delta \mathbf{k}) = E_n(\mathbf{k}_0) + \frac{\hbar^2}{2} \delta k_i \left(\mathsf{m}_n^{-1} \right)_{ij} \delta k_j \qquad \text{(in terms of } \mathsf{m})$$

Effective Mass Tensor in Terms of Velocity

$$\left[\mathsf{m}_n^{-1}(\mathbf{k}) \right]_{ij} = \pm \frac{1}{\hbar^2} \frac{\partial^2 E_n(\mathbf{k})}{\partial k_i \partial k_j} \qquad \text{(review: effective mass tensor)}$$
$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_n(\mathbf{k}) \qquad \text{(review: Bloch electron velocity)}$$
$$\left[\mathbf{v}_n(\mathbf{k}) \right]_i = \frac{1}{\hbar} \frac{\partial}{\partial k_i} E_n(\mathbf{k}) \qquad \text{(by components)}$$

Recognize expression for $\mathbf{v}_n$ in effective mass tensor to get...

$$\left[\mathsf{m}_n^{-1}(\mathbf{k}) \right]_{ij} = \pm \frac{1}{\hbar} \frac{\partial}{\partial k_j} \left[\mathbf{v}_n(\mathbf{k}) \right]_i \qquad \text{(in terms of } \mathbf{v}_n)$$
$$\mathsf{m}_n^{-1}(\mathbf{k}) = \pm \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{v}_n(\mathbf{k}) \qquad \text{(in vector form)}$$

Dynamics in Terms of Effective Mass Tensor

$$\hbar \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} = -e_0 (\boldsymbol{\mathcal{E}} + \mathbf{v}_n \times \mathbf{B}) \quad \text{(review: dynamics of Bloch electron)}$$
$$\mathsf{m}_n^{-1}(\mathbf{k}) = \pm \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{v}_n(\mathbf{k}) \qquad \text{(review: } \mathsf{m} \text{ in terms of } \mathbf{v}_n(\mathbf{k}))$$
$$\mathbf{a}_n = \frac{\mathrm{d}\mathbf{v}_n(\mathbf{k})}{\mathrm{d}t} \qquad \text{(acceleration of Bloch electron)}$$
$$= \nabla_{\mathbf{k}} \mathbf{v}_n(\mathbf{k}) \cdot \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} \qquad \text{(using the chain rule)}$$
$$= \pm \hbar \mathsf{m}_n^{-1} \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} \qquad \text{(using } \mathsf{m}^{-1} = \pm \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{v})$$
$$\mathsf{m}_n \mathbf{a}_n = \pm \hbar \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} \qquad \text{(rearranged)}$$
$$= \mp e_0 (\boldsymbol{\mathcal{E}} + \mathbf{v}_n \times \mathbf{B}) \qquad \text{(result: dynamics in terms of } \mathsf{m})$$

Important: expressions involving the effective mass tensor hold only if charge carrier energy is well-approximated by a quadratic expansion of the electron dispersion relation $E_n(\mathbf{k})$!

Electron Dispersions Near Conduction Band Minima

Consider the behavior of electrons at the minimum of a conduction band. Assume the band has minimum E_c at $\mathbf{k} = \mathbf{0}$.

$$E_{\mathrm{cb}}(\mathbf{k}) = E_c + \frac{\hbar^2}{2} k_i \left(\mathsf{m}_c \right)^{-1} k_j \qquad \text{(conduction band dispersion)}$$

Work in the mass tensor's system of principle axes...

$$\mathsf{m}_c = \begin{pmatrix} m_{c_1}^* & 0 & 0 \\ 0 & m_{c_2}^* & 0 \\ 0 & 0 & m_{c_3}^* \end{pmatrix} \qquad \text{(in system of principle axes)}$$

$$\mathsf{m}_c^{-1} = \begin{pmatrix} \frac{1}{m_{c_1}^*} & 0 & 0 \\ 0 & \frac{1}{m_{c_2}^*} & 0 \\ 0 & 0 & \frac{1}{m_{c_3}^*} \end{pmatrix} \qquad \text{(in system of principle axes)}$$

$m_{c_i}^*$ are the effective mass tensor's eigenvalues

$$E_{\mathrm{cb}}(\mathbf{k}) = E_c + \frac{\hbar^2}{2} \left(\frac{k_1^2}{m_{c_1}^*} + \frac{k_2^2}{m_{c_2}^*} + \frac{k_3^2}{m_{c_3}^*} \right) \qquad \text{(in system of PA)}$$

Hole Dispersions Near Valence Band Maxima

Consider the behavior of holes at the maximum of a valence band. Assume the band has maximum E_v at $\mathbf{k} = \mathbf{0}$.

$$E_{\mathrm{vb}}(\mathbf{k}) = E_v - \frac{\hbar^2}{2} k_i \left(\mathsf{m}_v \right)^{-1} k_j \qquad \text{(valence band dispersion)}$$

Work in the mass tensor's system of principle axes...

$$\mathsf{m}_v = \begin{pmatrix} m_{v_1}^* & 0 & 0 \\ 0 & m_{v_2}^* & 0 \\ 0 & 0 & m_{v_3}^* \end{pmatrix} \qquad \text{(in system of principle axes)}$$

$$\mathsf{m}_{\mathrm{v}}^{-1} = \begin{pmatrix} \frac{1}{m_{\mathrm{v}_1}^*} & 0 & 0 \\ 0 & \frac{1}{m_{\mathrm{v}_2}^*} & 0 \\ 0 & 0 & \frac{1}{m_{\mathrm{v}_3}^*} \end{pmatrix} \qquad \text{(in system of principle axes)}$$

$m_{\mathrm{v}_i}^*$ are the effective mass tensor's eigenvalues

$$E_{\mathrm{vb}}(\mathbf{k}) = E_{\mathrm{v}} - \frac{\hbar^2}{2} \left(\frac{k_1^2}{m_{\mathrm{v}_1}^*} + \frac{k_2^2}{m_{\mathrm{v}_2}^*} + \frac{k_3^2}{m_{\mathrm{v}_3}^*} \right) \qquad \text{(in system of PA)}$$

Semiconductors

Insulators, Semiconductors, and Conductors

Review:

- Fully-occupied electron energy bands do not carry either electric current or heat current.

- Consequence: only partially-filled bands should be considered in determined a solid's insulating properties.

$\implies$ Materials with only full ground-state bands are insulators.

$\implies$ Materials with some partially-filled ground-state bands are conductors.

New terminology:

- An insulator's *valence band* is the highest filled ground state energy band.

- An insulator's *conduction band* is the lowest empty ground state energy band.

- An insulator's *band gap* E_g is the energy difference between the maximum energy in the valence band and the minimum energy in the conduction band.

Semiconductors are ground-state insulators with a small-enough band gap that appreciable conduction due to thermal excitation can occur at temperatures $T > 0\,\mathrm{K}$ (but below the material's melting point).

$E_g \lesssim 1\,\mathrm{eV}$ (typical semiconductor band gap)
$E_g \gtrsim 5\,\mathrm{eV}$ (typical insulator band gap)
$k_B T \sim 0.025\,\mathrm{eV}$ at $T \sim 300\,\mathrm{K}$ (for reference)

Classes of Semiconductors:

- In *intrinsic* semiconductors, conduction is dominated by electrons thermally excited from VB to CB.

- In *extrinsic* semiconductors, conduction is dominated by electrons excited into the CB (or captured from the VB) from energy levels of impurities in the SC crystal.

  Extrinsic SC are often called *doped* semiconductors.

- In *homogeneous* SC, the concentration of impurities is uniform throughout the crystal.

- In *inhomogeneous*, concentration of impurities varies throughout the crystal, often in a carefully controlled way designed to produce desirable electronic properties.

Homogeneous Semiconductors

Carrier Densities in Homogeneous SC

Goal: derive expressions for the number densities of charge carriers in a homogeneous SC's valence and conduction bands.

Review: Fermi Function

$f(E) = \frac{1}{1+e^{\beta(E-\mu)}}$ (**Fermi function**)

Interpretation: the Fermi function gives the probability that a single-electron level with energy E in a system with chemical potential μ is occupied at temperature $T = 1/(k_B \beta)$.

$1 - f(E) = \frac{1}{1+e^{\beta(\mu-E)}}$ (useful identity)

Meaning of Common Symbols Used Below

E_c is the minimum of the conduction band
E_v is the maximum of the valence band
g_c is the density of levels for conduction band electrons
g_v is the density of levels for valence band holes
n_c is density of electrons in the conduction band
p_v is density of holes in the valence band

Electron and Hole Number Densities

$n_c = \int_{-\infty}^{\infty} g_c(E) f(E)\, dE$ (from first principles)

$ = \int_{E_c}^{\infty} g_c(E) f(E)\, dE$ (CB occupied only above E_c)

$ = \int_{E_c}^{\infty} \frac{g_c(E)}{1+e^{\beta(E-\mu)}}\, dE$ (substituting in $f(E)$)

$p_v = \int_{-\infty}^{\infty} g_v(E) \big[1 - f(E)\big]\, dE$ (from first principles)

$ = \int_{-\infty}^{E_v} g_c(E) \big[1 - f(E)\big]\, dE$ (VB occupied only up to E_v)

$ = \int_{-\infty}^{E_v} \frac{g_v(E)}{1+e^{\beta(\mu-E)}}\, dE$ (substituting in $1 - f(E)$)

On using $\big[1 - f(E)\big]$: $f(E)$ applies to electrons (not holes); every e^- moving from VB to CB leaves behind one hole in VB $\implies$ the occupation probability for holes in VB is the complement of the occupation probability for e^- in CB.

$E_c > \mu$ (follows from requiring $n_c \to 0$ as $T \to 0\,\mathrm{K}$)
$E_v < \mu$ (follows from requiring $p_v \to 0$ as $T \to 0\,\mathrm{K}$)
$\implies E_v < \mu < E_c$ (chemical potential lies in band gap)

Non-Degenerate Semiconductor Approximation

The non-degenerate semiconductor approximation assumes the chemical potential obeys the two conditions...

$E_c - \mu \gg k_B T$ (**non-degenerate SC approximation**)
$\mu - E_v \gg k_B T$ (**non-degenerate SC approximation**)

Interpretation: on a scale of thermal energy $k_B T$, the chemical potential lies deep in the SC's energy band gap, i.e. far from both the CB minimum and VB maximum.

Electron Density in the Non-Degenerate SC Approx.

$f(E) = \frac{1}{1+e^{\beta(E-\mu)}} \approx e^{-\beta(E-\mu)}$ (if $E_c - \mu \gg k_B T$)

$n_c = \int_{E_c}^{\infty} g_c(E) f(E)\, dE$ (in general)

$ \approx \int_{E_c}^{\infty} g_c(E) e^{-\beta(E-\mu)}\, dE$ (if $E_c - \mu \gg k_B T$)

$ = e^{-\beta(E_c-\mu)} \int_{E_c}^{\infty} g_c(E) e^{-\beta(E-E_c)}\, dE$ (factoring exponent)

$ \equiv e^{-\beta(E_c-\mu)} N_c(T)$ (defining N_c)

$N_c(T) \equiv \int_{E_c}^{\infty} g_c(E) e^{-\beta(E-E_c)}\, dE$ (definition of N_c)

Hole Density in the Non-Degenerate SC Approx.

$1 - f(E) = \frac{1}{1+e^{\beta(\mu-E)}} \approx e^{-\beta(\mu-E)}$ (if $\mu - E_v \gg k_B T$)

$p_v = \int_{-\infty}^{E_v} g_v(E) f(E)\, dE$ (in general)

$ \approx \int_{-\infty}^{E_v} g_v(E) e^{-\beta(\mu-E)}\, dE$ (if $\mu - E_v \gg k_B T$)

$ = e^{-\beta(\mu-E_v)} \int_{-\infty}^{E_v} g_v(E) e^{-\beta(E_v-E)}\, dE$ (factoring exponent)

$ \equiv e^{-\beta(\mu-E_v)} P_v(T)$ (defining P_v)

$P_v(T) \equiv \int_{-\infty}^{E_v} g_v(E) e^{-\beta(E_v-E)}\, dE$ (definition of P_v)

Conduction and Valence Band Dispersion Relations

Motivation: evaluating N_c and P_v requires expressions for the densities of state g_c and g_v, and finding g_c and g_v requires the CB and VB dispersion relations $E_{cb}(\mathbf{k})$ and $E_{vb}(\mathbf{k})$.

Assumptions[0.3ex]

(i) electrons occupy levels in the neighborhood of the conduction band minimum

(ii) holes occupy levels in the neighborhood of the valence band maximum

(iii) both the CB and VB effective mass tensors have three equal eigenvalues

Important: assuming holes and e^- occupy states in energy band extrema permits expanding the energy band dispersion relations as in Electron Dispersion Near CB Minima and Hole Dispersion Near VB Maxima.

$E_{cb}(\mathbf{k}) = E_c + \frac{\hbar^2}{2} k_i \big(\mathsf{m}_c^{-1}\big)_{ij} k_j$ (conduction band dispersion)

$$= E_{\rm c} + \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_{\rm c_1}^*} + \frac{k_2^2}{m_{\rm c_2}^*} + \frac{k_3^2}{m_{\rm c_3}^*}\right) \quad \text{(in m's system of PA)}$$

$$= E_{\rm c} + \frac{\hbar^2 k^2}{2m_{\rm c}^*} \quad \text{(assuming three equal eigenvalues)}$$

$$E_{\rm vb}(\mathbf{k}) = E_{\rm v} - \frac{\hbar^2}{2}k_i\left(\mathsf{m}_{\rm v}^{-1}\right)_{ij}k_j \quad \text{(valence band dispersion)}$$

$$= E_{\rm v} - \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_{\rm v_1}^*} + \frac{k_2^2}{m_{\rm v_2}^*} + \frac{k_3^2}{m_{\rm v_3}^*}\right) \quad \text{(in m's system of PA)}$$

$$= E_{\rm v} - \frac{\hbar^2 k^2}{2m_{\rm v}^*} \quad \text{(assuming three equal eigenvalues)}$$

Expressions for Densities of State

$$E_{\rm free}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad \text{(review: free electron dispersion)}$$

$$E_{\rm cb}(\mathbf{k}) = E_{\rm c} + \frac{\hbar^2 k^2}{2m_{\rm c}^*} \quad \text{(review: CB dispersion)}$$

$$E_{\rm vb}(\mathbf{k}) = E_{\rm v} - \frac{\hbar^2 k^2}{2m_{\rm v}^*} \quad \text{(review: VB dispersion)}$$

Important: the free e^- dispersion takes the same functional form as the CB and VB dispersion. The difference are:

(i) shift in energy by $E_{\rm c}$ or $E_{\rm v}$

(ii) electron m replaced by $m_{\rm c}^*$ or $m_{\rm v}^*$

$\implies$ we find the CB and VB densities of state by shifting the free e^- DOS by $E_{\rm c}$ or $E_{\rm v}$ and replacing m with $m_{\rm c}^*$ or $m_{\rm v}^*$.

$$g_{\rm free}(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E} \quad \text{(review: free electron DOS)}$$

$$g_{\rm c}(E) = \frac{1}{2\pi^2}\left(\frac{2m_{\rm c}^*}{\hbar^2}\right)^{3/2}\sqrt{|E_{\rm c} - E|} \quad \textbf{(CB density of state)}$$

$$g_{\rm v}(E) = \frac{1}{2\pi^2}\left(\frac{2m_{\rm v}^*}{\hbar^2}\right)^{3/2}\sqrt{|E_{\rm v} - E|} \quad \textbf{(VB density of state)}$$

Note: for an effective mass tensor with different eigenvalues m_1^*, m_2^*, m_3^*, replace $m_{\rm c}^*$ or $m_{\rm v}^*$ with...

$$(m_{\rm c}^*)^{3/2} \to (m_{\rm c_1}^*, m_{\rm c_2}^*, m_{\rm c_3}^*) \quad \text{(for } \mathsf{m}_{\rm c} \text{ with different eigvals.)}$$

$$(m_{\rm v}^*)^{3/2} \to (m_{\rm v_1}^*, m_{\rm v_2}^*, m_{\rm v_3}^*) \quad \text{(for } \mathsf{m}_{\rm v} \text{ with different eigvals.)}$$

Evaluating $N_{\rm c}$

$$N_{\rm c}(T) = \int_{E_{\rm c}}^{\infty} g_{\rm c}(E)e^{-\beta(E-E_{\rm c})}\,{\rm d}E \quad \text{(from above)}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_{\rm c}^*}{\hbar^2}\right)^{3/2}\int_{E_{\rm c}}^{\infty} e^{-\beta(E-E_{\rm c})}\sqrt{|E_{\rm c} - E|}\,{\rm d}E$$

Let $x \equiv \beta(E - E_{\rm c})$ (new integration variable)

$$N_{\rm c}(T) = \frac{\sqrt{2}}{\pi^2}\left(\frac{m_{\rm c}^* k_{\rm B}T}{\hbar^2}\right)^{3/2}\int_0^{\infty}\sqrt{x}e^{-x}\,{\rm d}x \quad \text{(in terms of } x)$$

$$\int_0^{\infty}\sqrt{x}e^{-x}\,{\rm d}x = \Gamma(3/2) = \frac{\sqrt{\pi}}{2} \quad \text{(using the gamma function)}$$

$$N_{\rm c}(T) = \frac{1}{4}\left(\frac{2m_{\rm c}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2} \quad \text{(result for } N_{\rm c})$$

Evaluating $P_{\rm v}$

$$P_{\rm v}(T) = \int_{-\infty}^{E_{\rm v}} g_{\rm v}(E)e^{-\beta(E_{\rm v}-E)}\,{\rm d}E \quad \text{(from above)}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_{\rm v}^*}{\hbar^2}\right)^{3/2}\int_{-\infty}^{E_{\rm v}} e^{-\beta(E_{\rm v}-E)}\sqrt{|E_{\rm v} - E|}\,{\rm d}E$$

Let $x \equiv \beta(E_{\rm v} - E)$ (new integration variable)

$$P_{\rm v}(T) = \frac{\sqrt{2}}{\pi^2}\left(\frac{m_{\rm v}^* k_{\rm B}T}{\hbar^2}\right)^{3/2}\int_0^{\infty}\sqrt{x}e^{-x}\,{\rm d}x \quad \text{(in terms of } x)$$

$$\int_0^{\infty}\sqrt{x}e^{-x}\,{\rm d}x = \Gamma(3/2) = \frac{\sqrt{\pi}}{2} \quad \text{(using the gamma function)}$$

$$P_{\rm v}(T) = \frac{1}{4}\left(\frac{2m_{\rm v}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2} \quad \text{(result for } P_{\rm v})$$

Summary of Results: Charge Carrier Densities

$$n_e = \int_{E_{\rm c}}^{\infty} g(E)f(E)\,{\rm d}E \quad \text{(in general)}$$

$$p_{\rm v} = \int_{-\infty}^{E_{\rm v}} f(E)g(E)\,{\rm d}E \quad \text{(in general)}$$

What follows assumes $E_{\rm c} - \mu \gg k_{\rm B}T$ and $\mu - E_{\rm v} \gg k_{\rm B}T$!

$$n_{\rm c} \approx e^{-\beta(E_{\rm c}-\mu)}N_{\rm c}(T)$$

$$p_{\rm v} \approx e^{-\beta(\mu-E_{\rm v})}P_{\rm v}(T)$$

$$N_{\rm c}(T) = \frac{1}{4}\left(\frac{2m_{\rm c}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2}$$

$$P_{\rm v}(T) = \frac{1}{4}\left(\frac{2m_{\rm v}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2}$$

$$n_{\rm c} = \frac{1}{4}\left(\frac{2m_{\rm c}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2}e^{-\beta(E_{\rm c}-\mu)} \quad \textbf{(approx. CB } e^- \textbf{ density)}$$

$$p_{\rm v} = \frac{1}{4}\left(\frac{2m_{\rm v}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2}e^{-\beta(\mu-E_{\rm v})} \quad \textbf{(approx. VB hole density)}$$

Intrinsic Semiconductors

Review: in intrinsic semiconductors, conduction is dominated by electrons thermally excited from VB to CB.

Concept: In intrinsic SC, every electron excited into the CB from the VB leaves behind a hole in the VB.

$$\implies n_{\rm c} = p_{\rm v} \quad \text{(in intrinsic semiconductors)}$$

Interpretation: The equality $n_{\rm c} = p_{\rm v}$ expresses conservation of total electron number in intrinsic semiconductors.

Assumption: the content of this section implicitly assumes the non-degenerate semiconductor approximation!

Intrinsic Charge Carrier Density

The equality of $n_{\rm c}$ and $p_{\rm v}$ in intrinsic semiconductors motivates the definition of an *intrinsic carrier density* $n_{\rm i}$ given by...

$$n_{\rm c} \equiv n_{\rm i} \equiv p_{\rm v} \quad \textbf{(intrinsic carrier density)}$$

$$n_{\rm i}^2 = n_{\rm c}p_{\rm v} = N_{\rm c}P_{\rm v}e^{-\beta(E_{\rm c}-E_{\rm v})} \quad \text{(from above } n_{\rm c} \text{ and } p_{\rm v})$$

$$= N_{\rm c}P_{\rm v}e^{-\beta E_{\rm g}} \quad \text{(since } E_{\rm g} = E_{\rm c} - E_{\rm v})$$

$$\implies n_{\rm i} = \sqrt{N_{\rm c}P_{\rm v}}e^{-\frac{\beta E_{\rm g}}{2}}$$

Chemical Potential in Intrinsic Semiconductors

Goal: find an expression for the temperature dependence $\mu(T)$ of an intrinsic semiconductor's chemical potential.

$$n_{\rm c} = p_{\rm v} \quad \text{(by definition of intrinsic SC)}$$

$$n_{\rm c} = p_{\rm v} \implies N_{\rm c}e^{-\beta(E_{\rm c}-\mu)} = P_{\rm v}e^{-\beta(\mu-E_{\rm v})}$$

$$e^{-\beta(E_{\rm c}-\mu)} = \frac{P_{\rm v}}{N_{\rm c}}e^{-\beta(\mu-E_{\rm v})} \quad \text{(rearranged)}$$

$$-\beta(E_{\rm c} - \mu) = \ln\frac{P_{\rm v}}{N_{\rm c}} - \beta(\mu - E_{\rm v}) \quad \text{(taking logarithm)}$$

$$= \frac{3}{2}\ln\frac{m_{\rm v}^*}{m_{\rm c}^*} - \beta(\mu - E_{\rm v}) \quad \text{(using } \frac{P_{\rm v}}{N_{\rm c}} = \left(\frac{m_{\rm v}^*}{m_{\rm c}^*}\right)^{3/2})$$

$$\mu(T) = \frac{1}{2}(E_{\rm c} + E_{\rm v}) + \frac{3}{4}k_{\rm B}T\ln\frac{m_{\rm v}^*}{m_{\rm c}^*} \quad \text{(solving for } \mu)$$

Finally, use $E_{\rm c} = E_{\rm v} + E_{\rm g} \implies E_{\rm c} + E_{\rm v} = 2E_{\rm v} + E_{\rm g}$ to get...

$$\mu(T) = E_{\rm v} + \frac{E_{\rm g}}{2} + \frac{3}{4}k_{\rm B}T\ln\frac{m_{\rm v}^*}{m_{\rm c}^*} \quad \textbf{(chem. pot. of an ISC)}$$

Interpretation: Chemical Potential in Intrinsic SC

$$\mu(T) = E_{\rm v} + \frac{E_{\rm g}}{2} + \frac{3}{4}k_{\rm B}T\ln\frac{m_{\rm v}^*}{m_{\rm c}^*} \quad \text{(for review)}$$

$$E_{\rm F} \equiv \mu(T)\big|_{T=0\,{\rm K}} = E_{\rm v} + \frac{E_{\rm g}}{2} \quad \text{(Fermi energy in ISC)}$$

Conclusion: an intrinsic semiconductor's Fermi energy lies exactly in the middle of the band gap.

$$m_{\rm v}^* \sim m_{\rm c}^* \quad \text{(in typical materials and conditions)}$$

$$\implies \ln\frac{m_{\rm v}^*}{m_{\rm c}^*} \lesssim 1 \quad \text{(since } m_{\rm v}^* \sim m_{\rm c}^*)$$

$$\implies \frac{3}{4}k_{\rm B}T\ln\frac{m_{\rm v}^*}{m_{\rm c}^*} \lesssim k_{\rm B}T \quad \text{(since } \ln\frac{m_{\rm v}^*}{m_{\rm c}^*} \lesssim 1)$$

Conclusion: the non-zero temperature deviation of $\mu(T)\big|_{T>0}$ away from $E_{\rm F} = E_{\rm v} + \frac{E_{\rm g}}{2}$ is of the order $k_{\rm B}T$.

Consequence: at temperatures for which $k_{\rm B}T \ll E_{\rm g}$, an intrinsic semiconductor obeys $\mu(T) \approx E_{\rm g}$, and the non-degenerate semiconductor approximation $E_{\rm c} - \mu \ll k_{\rm B}T$ and $\mu - E_{\rm v} \ll k_{\rm B}T$ is an excellent approximation.

Doped Homogeneous Semiconductors

Review: in extrinsic (aka doped) SC, conduction is dominated by electrons excited into the CB (or captured from the VB) from energy levels of impurities in the SC crystal.

Assumption: the content of this section implicitly assumes the non-degenerate semiconductor approximation!

For Orientation: Typical Carrier Densities

$$n_{\rm pure} \sim 5 \cdot 10^{22}\,{\rm cm}^{-3} \quad \text{(atom density in pure Si)}$$

$$n_{\rm i} \sim 10^{10}\,{\rm cm}^{-3} \quad \text{(intrinsic density in Si at } T \sim 300\,{\rm K})$$

$$N_{\rm d}, N_{\rm a} \sim 10^{13}\,{\rm cm}^{-3} \text{ to } 10^{18}\,{\rm cm}^{-3} \quad \text{(typical dopant densities)}$$

Some General Considerations

Doped semiconductors are characterized by the relationships...

$$n_{\rm c} - p_{\rm v} \neq 0 \quad \text{(in doped semiconductors)}$$

$$n_{\rm c}p_{\rm v} = n_{\rm i}^2 \quad \text{(in doped semiconductor)}$$

$$\mu_{\mathrm{i}}(T) \equiv E_{\mathrm{v}} + \frac{E_{\mathrm{g}}}{2} + \frac{3}{4}\ln\frac{m_{\mathrm{v}}^*}{m_{\mathrm{c}}^*} \qquad \text{(in intrinsic SC)}$$
$$\mu(T) \neq \mu_{\mathrm{i}}(T) \qquad \text{(in doped SC)}$$

Carrier Densities in Doped Semiconductors

Goal: derive expressions for charge carrier densities in the valence and conduction bands of doped homogeneous SCs.

Differences in Carrier Densities vs. Intrinsic SC

Differences between intrinsic and doped SC may arise from...

(i) different effective masses m_{c}^* and m_{v}^* (via N_{c} and P_{v})

(ii) different energy levels E_{v} and E_{c}

(iii) different chemical potential μ

Concept: effective mass and the energy levels E_{v} and E_{c} depend on the semiconductor's underlying lattice structure. Since dopant concentrations are typically orders of magnitude less than intrinsic ion concentrations, doped and intrinsic SC crystal structures are essentially identical.

Conclusion: carrier densities in doped and intrinsic SC differ appreciably only because of changes in chemical potential μ!
$$N_{\mathrm{c}}^{(\mathrm{d})} \approx N_{\mathrm{c}}^{(\mathrm{i})} \text{ and } P_{\mathrm{v}}^{(\mathrm{d})} \approx P_{\mathrm{v}}^{(\mathrm{i})} \qquad \text{(due to low dopant densities)}$$
$$n_{\mathrm{c}} = N_{\mathrm{c}}(T)e^{-\beta(E_{\mathrm{c}}-\mu)}, \ \mu \neq \mu_{\mathrm{i}} \qquad \text{(in doped SC)}$$
$$p_{\mathrm{v}} = P_{\mathrm{v}}(T)e^{-\beta(\mu-E_{\mathrm{v}})}, \ \mu \neq \mu_{\mathrm{i}} \qquad \text{(in doped SC)}$$

Extrinsic Carrier Densities I: CB Electrons

$$\text{Let } \Delta n \equiv n_{\mathrm{c}} - p_{\mathrm{v}} \qquad \text{(difference in carrier densities)}$$
$$n_{\mathrm{c}}^2 - p_{\mathrm{v}}n_{\mathrm{c}} = n_{\mathrm{c}}\Delta n \qquad \text{(multiplying through by } n_{\mathrm{c}})$$
$$n_{\mathrm{c}}^2 - n_{\mathrm{c}}\Delta n - n_{\mathrm{i}}^2 = 0 \qquad \text{(using } n_{\mathrm{i}}^2 = p_{\mathrm{v}}n_{\mathrm{c}})$$
$$n_{\mathrm{c}} = \frac{1}{2}\left[\Delta n \pm \sqrt{\Delta n^2 + 4n_{\mathrm{i}}^2}\right] \qquad \text{(quadratic formula)}$$
$$= \frac{1}{2}\left[\Delta n + \sqrt{\Delta n^2 + 4n_{\mathrm{i}}^2}\right] \qquad \text{(use positive solution so } n_{\mathrm{c}} > 0)$$

Extrinsic Carrier Densities II: VB Holes

$$\Delta n = n_{\mathrm{c}} - p_{\mathrm{v}} \qquad \text{(difference in carrier densities)}$$
$$n_{\mathrm{c}}p_{\mathrm{v}} - p_{\mathrm{v}}^2 = p_{\mathrm{v}}\Delta n \qquad \text{(multiplying through by } p_{\mathrm{v}})$$
$$p_{\mathrm{v}}^2 + p_{\mathrm{v}}\Delta n - n_{\mathrm{i}}^2 = 0 \qquad \text{(using } n_{\mathrm{i}}^2 = n_{\mathrm{c}}p_{\mathrm{v}})$$
$$p_{\mathrm{v}} = \frac{1}{2}\left[-\Delta n \pm \sqrt{\Delta n^2 + 4n_{\mathrm{i}}^2}\right] \qquad \text{(quadratic formula)}$$
$$= \frac{1}{2}\left[\sqrt{\Delta n^2 + 4n_{\mathrm{i}}^2} - \Delta n\right] \qquad \text{(use positive solution so } p_{\mathrm{v}} > 0)$$

Explicit Expression for Density Difference Δn

$$n_{\mathrm{c}} = N_{\mathrm{c}}e^{-\beta(E_{\mathrm{c}}-\mu)} \qquad \text{(in doped SC)}$$
$$n_{\mathrm{i}} = N_{\mathrm{c}}e^{-\beta(E_{\mathrm{c}}-\mu_{\mathrm{i}})} \qquad \text{(in intrinsic SC)}$$
$$\implies n_{\mathrm{c}} = n_{\mathrm{i}}e^{\beta(\mu-\mu_{\mathrm{i}})} \qquad \text{(dividing } n_{\mathrm{c}} \text{ by } n_{\mathrm{i}})$$
$$p_{\mathrm{v}} = P_{\mathrm{v}}e^{-\beta(\mu-E_{\mathrm{v}})} \qquad \text{(in doped SC)}$$
$$n_{\mathrm{i}} = P_{\mathrm{v}}e^{-\beta(\mu_{\mathrm{i}}-E_{\mathrm{v}})} \qquad \text{(in intrinsic SC)}$$
$$\implies p_{\mathrm{v}} = n_{\mathrm{i}}e^{-\beta(\mu-\mu_{\mathrm{i}})} \qquad \text{(dividing } p_{\mathrm{v}} \text{ by } n_{\mathrm{i}})$$
$$\Delta n = n_{\mathrm{c}} - p_{\mathrm{v}} \qquad \text{(by definition)}$$
$$= n_{\mathrm{i}}\left[e^{\beta(\mu-\mu_{\mathrm{i}})} - e^{-\beta(\mu-\mu_{\mathrm{i}})}\right] \qquad \text{(from just-derived } n_{\mathrm{c}} \text{ and } p_{\mathrm{v}})$$
$$= 2n_{\mathrm{i}}\sinh\left[\beta(\mu - \mu_{\mathrm{i}})\right] \qquad \text{(result: difference in densities)}$$

Dopant Energy Levels

Review: Hydrogen Atom Electrons

The distance and binding energy scale of an atomic electron in an *isolated* hydrogen atom are of the scale...

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e_0^2} \approx 0.05\,\mathrm{nm} \qquad \text{(Bohr radius; distance scale)}$$
$$1\,\mathrm{Ry} = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6\,\mathrm{eV} \qquad \text{(Rydberg energy; energy scale)}$$

Group III		Group IV		Group V	
Al	$3\mathrm{s}^2\,3\mathrm{p}^1$	Si	$3\mathrm{s}^2\,3\mathrm{p}^2$	P	$3\mathrm{s}^2\,3\mathrm{p}^3$
Ga	$4\mathrm{s}^2\,4\mathrm{p}^1$	Ge	$4\mathrm{s}^2\,4\mathrm{p}^2$	As	$4\mathrm{s}^2\,4\mathrm{p}^3$

Model for Levels of Donor Impurities

- Begin with a pure (intrinsic) semiconductor crystal made with volume density N_{pure} of group IV elements.

- Distribute group V donor impurities with donor density $N_{\mathrm{D}} \ll N_{\mathrm{pure}}$ throughout the pure crystal; assume donor density is low enough that every donor is surrounded by very many group IV atoms.

- Model donor impurities as a group IV atom with one additional proton (fixed at the nucleus) and one additional donor electron (which may be ionized).

Concept: the donor electron in an *isolated* donor atom would have ionization energy $1\,\mathrm{Ry} \sim 10\,\mathrm{eV}$, but a donor electron embedded in a surrounding group IV lattice has greatly reduced binding energy because...

1. The electric field of the positive nucleus binding the donor e^- is reduced by the SC's dielectric constant $\epsilon \sim 15$.

2. The donor electron mass is replaced by effective electron mass $m^* \sim 0.1m_e$.

Conclusion: model donor electron and additional proton as a free electron of effective mass m^* in the presence of a scaled attractive proton charge e_0/ϵ.
Replace m_e with m^* and ϵ_0 with $\epsilon\epsilon_0$ in the expressions for a_0 and $1\,\mathrm{Ry}$ to get...
$$r_0 \sim \frac{m_e}{m^*}\epsilon \cdot a_0 \sim 100a_0 \qquad \text{(donor } e^- \text{ distance scale)}$$
$$E_{\mathrm{b}} = \frac{m^*}{m_e}\frac{1}{\epsilon^2}\cdot\mathrm{Ry} \sim 0.0005\,\mathrm{Ry} \qquad \text{(donor } e^- \text{ binding energy)}$$
Conclusion: donor electrons have a far greater range and far lower binding energy than an e^- in an isolated hydrogen atom.
$$E_{\mathrm{b}} \sim 0.0005\,\mathrm{eV} \text{ to } 0.01\,\mathrm{eV} \quad \text{(typical donor } e^- \text{ binding energy)}$$
$$k_{\mathrm{B}}T\big|_{T\sim300\,\mathrm{K}} \sim 0.025\,\mathrm{eV} \gg E_{\mathrm{b}} \qquad (k_{\mathrm{B}}T \text{ at room temp.)}$$
Result: donor electrons are easily freed from their donor ion cores as a result of room-temperature thermal fluctuations!

Model for Levels of Acceptor Impurities

Replace group V donor impurities with group III acceptor impurities and donor electron with acceptor hole. The resulting ideas are analogous.
$$E_{\mathrm{b}} \sim 0.0005\,\mathrm{eV} \text{ to } 0.01\,\mathrm{eV} \qquad \text{(typical acceptor hole } E_{\mathrm{b}})$$
$$k_{\mathrm{B}}T\big|_{T\sim300\,\mathrm{K}} \sim 0.025\,\mathrm{eV} \gg E_{\mathrm{b}} \qquad (k_{\mathrm{B}}T \text{ at room temp.)}$$
Result: acceptor holes are easily freed from their acceptor ion cores as a result of room-temperature thermal fluctuations!

Energy Levels

The small binding energy for dopant charge carriers produces two new energy levels in doped semiconductors:

1. A donor level E_{d} just below the conduction band E_{c},

2. an acceptor level E_{a} just above the valence band E_{v}.

The dopant binding dopant $E_{\mathrm{b}}^{(\mathrm{d})} = E_{\mathrm{c}} - E_{\mathrm{d}}$ and $E_{\mathrm{b}}^{(\mathrm{a})} = E_{\mathrm{a}} - E_{\mathrm{v}}$ are much less than the semiconductor band gap E_{g}, so dopant charge carrier are much more readily thermally excited than intrinsic charge carriers.

Occupation Statistics of Donor Levels

*

Review: Grand Canonical Ensemble Consider a system of non-interacting particles in thermodynamic equilibrium in contact with an external reservoir, with which the system may exchange both energy and particles.
μ is the system's chemical potential
Let j index the system's possible states
E_j is the energy of the j-th state
N_j is the number of particles occupying the j-th state
$$Z_{\mathrm{gc}} = \sum_j e^{-\beta(E_j - \mu N_j)} \qquad \text{(GC partition function)}$$

The average number $\langle n \rangle$ of particles in the system is...

$\langle n \rangle = \frac{1}{Z_{\text{gc}}} \sum_j N_j e^{-\beta(E_j - \mu N_j)}$

$\quad = \frac{\sum_j N_j e^{-\beta(E_j - \mu N_j)}}{\sum_j e^{-\beta(E_j - \mu N_j)}}$

Occupation Statistics of Donor Energy Levels

Consider a doped SC with donor density $N_{\text{d}} \ll N_{\text{pure}}$
Goal: compute the number density n_{d} of electrons bound to donor ion cores.
Assumption: assume donor density is low enough that donor electrons are *non-interacting*
$\implies$ n_{d} is the product of donor density N_{d} and the average donor electron occupation $\langle n \rangle$ of a single donor site.
Idea: express occupation of a single donor site with GC ensemble
Possible e^- occupation states of a single donor site are...

1. no occupation; $N = 0$, $E = 0$

2. occupation by one spin up electron; $N = 1$, $E = E_{\text{d}}$

3. occupation by one spin down electron; $N = 1$, $E = E_{\text{d}}$

4. occupation by two electrons with spin up and spin down; $N = 2$, $E = 2E_{\text{d}} + E_{\text{repulsion}}$

Neglect double-electron occupation because large electrostatic repulsion $E_{\text{repulsion}} \gg E_{\text{d}}$ makes occupation unlikely.

$Z_{\text{gc}} = \sum_j e^{-\beta(E_j - \mu N_j)}$

$\quad = 2 \cdot e^{-\beta(E_{\text{d}} - 1 \cdot \mu)} + e^{-\beta(0 - 0 \cdot \mu)}$

$\quad = 1 + e^{-\beta(E_{\text{d}} - \mu)}$

$\sum_j N_j e^{-\beta(E_j - \mu N_j)} = 2 \cdot (1 \cdot e^{-\beta(E_{\text{d}} - \mu)}) + 0 \cdot e^{-\beta \cdot 0}$

$\qquad\qquad = 2 e^{-\beta(E_{\text{d}} - \mu)}$

$\langle n \rangle = \frac{1}{Z_{\text{gc}}} \sum_j N_j e^{-\beta(E_j - \mu N_j)}$ (for a single donor site)

$\quad = \frac{2 e^{-\beta(E_{\text{d}} - \mu)}}{1 + 2 e^{-\beta(E_{\text{d}} - \mu)}}$ (using above Z_{gc} and sum)

$\quad = \frac{1}{1 + \frac{1}{2} e^{\beta(E_{\text{d}} - \mu)}}$ (simplified)

$n_{\text{d}} = \langle n \rangle N_{\text{d}}$ (assuming donor e^- are noninteracting)

$\quad = \frac{N_{\text{d}}}{1 + \frac{1}{2} e^{\beta(E_{\text{d}} - \mu)}}$ (**donor e^- occupation density**)

Occupation Statistics of Acceptor Energy Levels

Consider a doped SC with acceptor density $N_{\text{a}} \ll N_{\text{pure}}$
Goal: compute the number density p_{v} of holes bound to acceptor ion cores.
Assumption: assume acceptor density is low enough that donor holes are *non-interacting*
$\implies$ p_{a} is the product of acceptor density N_{a} and the average donor hole occupation $\langle p \rangle$ of a single acceptor site.
Idea: express *electron* occupation of one acceptor site with GC ensemble, then convert electron density to hole density
Possible e^-/hole occupation states of one acceptor site are...

1. occupation by two electrons of opposite spins/occupation by zero holes; $N = 2$, $E = 2E_{\text{a}}$

2. occupation by one spin up electron/occupation by one hole; $N = 1$, $E = E_{\text{a}}$

3. occupation by one spin down electron/occupation by one hole; $N = 1$, $E = E_{\text{a}}$

4. occupation by zero electrons/occupation by two holes; $N = 0$, $E = 0$.

Neglect double-hole/zero-electron occupation because large electrostatic repulsion $E_{\text{repulsion}} \gg E_{\text{a}}$ between two holes makes occupation unlikely.

$Z_{\text{gc}} = \sum_j e^{-\beta(E_j - \mu N_j)} = e^{-\beta(2 E_{\text{a}} - 2 \cdot \mu)} + 2 e^{-\beta(E_{\text{a}} - 1 \cdot \mu)}$

$\sum_j N_j e^{-\beta(E_j - \mu N_j)} = 2 \cdot e^{-\beta(2 E_{\text{a}} - 2\mu)} + 2 \cdot (1 \cdot e^{-\beta(E_{\text{a}} - \mu)})$

$\langle n \rangle = \frac{1}{Z_{\text{gc}}} \sum_j N_j e^{-\beta(E_j - \mu N_j)}$ (for *electrons* in acceptor levels)

$\quad = \frac{2 e^{-\beta(E_{\text{a}} - \mu)} + 2 e^{-2\beta(E_{\text{a}} - \mu)}}{2 e^{-\beta(E_{\text{a}} - \mu)} + e^{-2\beta(E_{\text{a}} - \mu)}}$

$\quad = \frac{2 + 2 e^{-\beta(E_{\text{a}} - \mu)}}{2 + e^{-\beta(E_{\text{a}} - \mu)}}$ (dividing by $e^{-\beta(E_{\text{a}} - \mu)}$)

$\langle p \rangle = 2 - \langle n \rangle$ (electron-hole occupation relationship)

$\quad = 2 \cdot \frac{2 + e^{-\beta(E_{\text{a}} - \mu)}}{2 + e^{-\beta(E_{\text{a}} - \mu)}} - \frac{2 + 2 e^{-\beta(E_{\text{a}} - \mu)}}{2 + e^{-\beta(E_{\text{a}} - \mu)}}$ (common denominator)

$\quad = \frac{1}{1 + \frac{1}{2} e^{\beta(\mu - E_{\text{a}})}}$ (simplifying)

$p_{\text{a}} = \langle p \rangle N_{\text{a}}$ (assuming acc. holes are noninteracting)

$\quad = \frac{N_{\text{a}}}{1 + \frac{1}{2} e^{\beta(\mu - E_{\text{a}})}}$ (**acc. hole occupation density**)

Carrier Concentrations in Doped SCs

Goal: analyze how the intrinsic semiconductor relationship $n_{\text{c}} = p_{\text{v}}$ generalizes to extrinsic semiconductor due to the addition of dopant energy levels.

Equilibrium Densities in a Doped SC if $N_{\text{d}} > N_{\text{a}}$

Consider an doped SC with dopant densities $N_{\text{d}} > N_{\text{a}}$.
Consider the SC's ground state configuration at $T = 0\,\text{K}$
At $T = 0\,\text{K}$, e^- will assume lowest possible energy configuration
$\implies$ N_{a} donor electrons drop into acceptor levels
At $T = 0\,\text{K}$ if $N_{\text{d}} > N_{\text{a}}$...

- Conduction band is fully empty

- Donor levels hold $N_{\text{d}} - N_{\text{a}}$ electrons (i.e. as empty as the $N_{\text{a}} < N_{\text{d}}$ available lower-energy acceptor levels allow)

- Acceptor levels are fully occupied with donor e^-

- Valence band is fully occupied with valence e^-

Summary: at $T = 0\,\text{K}$, acceptor/valence bands are full, and conduction/donor bands hold $N_{\text{d}} - N_{\text{a}}$ electrons.
Idea: in thermal equilibrium at $T > 0\,\text{K}$, electrons will be redistributed among these levels, but the total electron number in the SC is conserved!
Consequence: at $T > 0\,\text{K}$, the density $n_{\text{c}} + n_{\text{d}}$ of e^- in conduction and donor bands must exceed the $T = 0\,\text{K}$ value of $N_{\text{d}} - N_{\text{a}}$ by the number of e^- vacating the originally-full acceptor and valence bands, given by $p_{\text{v}} + p_{\text{a}}$.
$\implies n_{\text{c}} + n_{\text{d}} = N_{\text{d}} - N_{\text{a}} + p_{\text{v}} + p_{\text{a}}$ (**eq. densities in DSC**)

Equilibrium Densities in a Doped SC if $N_{\text{a}} > N_{\text{d}}$

Consider an doped SC with dopant densities $N_{\text{a}} > N_{\text{d}}$.
Note: result is the same as derived above if $N_{\text{d}} > N_{\text{a}}$, i.e.
$n_{\text{c}} + n_{\text{d}} = N_{\text{d}} - N_{\text{a}} + p_{\text{v}} + p_{\text{a}}$
This section is given just as an excercise/alternative perspective.

Consider the SC's ground state configuration at $T = 0\,\text{K}$
At $T = 0\,\text{K}$, e^- will assume lowest possible energy configuration
$\implies$ all N_{a} donor electrons drop into acceptor levels
At $T = 0\,\text{K}$ if $N_{\text{a}} > N_{\text{d}}$...

- Conduction band is fully empty

- Donor levels are fully empty

- Acceptor levels hold N_{d} electrons (or $N_{\text{a}} - N_{\text{d}}$ holes)

- Valence band is fully occupied with valence e^-

Summary: at $T = 0\,\text{K}$, conduction/donor bands are fully empty, and acceptor/valence bands hold $N_{\text{a}} - N_{\text{d}}$ holes.
Idea: in thermal equilibrium at $T > 0\,\text{K}$, electrons (holes) will be redistributed among these levels, but the total electron (hole) number in the SC is conserved!
Consequence: at $T > 0\,\text{K}$, the density $p_{\text{v}} + p_{\text{a}}$ of holes in valence and acceptor bands must exceed the $T = 0\,\text{K}$ value of $N_{\text{a}} - N_{\text{d}}$ by the number of electrons occupying the originally-empty donor and conduction bands, given by $n_{\text{c}} + n_{\text{d}}$.
$\implies p_{\text{a}} + p_{\text{v}} = N_{\text{a}} - N_{\text{d}} + n_{\text{c}} + n_{\text{d}}$ (same as for $N_{\text{d}} > N_{\text{a}}$!)

Dopant Carrier Concentrations at Room Temperature

Consider a doped SC at room temp. where $k_BT \sim 0.025\,\mathrm{eV}$

$E_b \sim 0.0005\,\mathrm{eV}$ to $0.01\,\mathrm{eV}$ (typical dopant binding energy)

$(E_c - E_d), (E_a - E_v) \sim E_b \ll k_BT$

These relationships, together with the implicit non-degenerate SC approximation, permit the following assumptions...

Assume: $E_d - \mu \gg k_BT$ (based on $E_c - E_d \ll k_BT$)

Assume: $\mu - E_a \gg k_BT$ (based on $E_a - E_v \ll k_BT$)

Interpretation: at room temperature, nearly all dopant e_- are thermally excited out the dopant levels (so $n_d \ll N_d$) and nearly all acceptor levels are filled with electrons thermally excited from valence band (so $p_a \ll N_a$).

$n_c - p_v \approx N_d - N_a$ **(room temp. densities in DSC)**

$n_c \approx p_v + N_d$ (n-type SC at room temp.)

$p_v \approx n_c + N_a$ (p-type SC at room temp.)

Fermi Energy and Chemical Potential In Doped SC

Review: a system's Fermi energy E_F is the energy of the highest-energy occupied electron level at $T = 0\,\mathrm{K}$.

$$E_F = \begin{cases} E_d & N_d > N_a \\ E_a & N_a > N_d \end{cases} \quad \text{(Fermi energy in doped SC)}$$

If $N_d > N_a$, the chemical potential falls from E_d towards the center of band gap with increasing temperature.

If $N_a > N_d$, the chemical potential grows from E_a towards the center of band gap with increasing temperature.

Heuristic explanation: typical dopant densities are many orders of magnitude less than densities of intrinsic atoms $\implies$ the doped SC chemical potential rapidly approaches the intrinsic SC chemical potential (which occurs near the band gap center) once thermal effects become appreciable.

Carrier Densities in Lightly-Doped Semiconductors

Consider a doped semiconductor in the room temperature limit where $E_d - \mu \gg k_BT$ and $\mu - E_a \gg k_BT$

$n_c - p_v \approx N_d - N_a$ (review: room temp. densities in DSC)

$\Delta n \equiv n_c - p_v$ (from Extrinsic Carrier Densities I)

$\Delta n \approx N_d - N_a$ (at room temp.)

$\Delta n \ll n_i$ (from assumption of light doping)

$n_c = \frac{1}{2}\left[\Delta n + \sqrt{\Delta n^2 + 4n_i^2}\right]$ (from Ext. Carrier Densities I)

$\quad \approx n_i + \frac{1}{2}(N_d - N_a) + \mathcal{O}(\Delta n)^2$ (for $\Delta n \ll n_i$)

$p_v = \frac{1}{2}\left[\sqrt{\Delta n^2 + 4n_i^2} - \Delta n\right]$ (from Ext. Carrier Densities II)

$\quad \approx n_i - \frac{1}{2}(N_d - N_a) + \mathcal{O}(\Delta n)^2$ (for $\Delta n \ll n_i$)

$\begin{Bmatrix} n_c \\ p_v \end{Bmatrix} \approx n_i \pm \frac{1}{2}(N_d - N_a)$ (limit of light doping)

Carrier Densities in Heavily-Doped Semiconductors

Consider a doped semiconductor in the room temperature limit where $E_d - \mu \gg k_BT$ and $\mu - E_a \gg k_BT$

$n_c - p_v \approx N_d - N_a$ (review: room temp. densities in DSC)

$\Delta n \equiv n_c - p_v$

$\Delta n \approx N_d - N_a$ (at room temp.)

$\Delta n \gg n_i$ (from assumption of heavy doping)

$n_c = \frac{1}{2}\left[\Delta n + \sqrt{\Delta n^2 + 4n_i^2}\right]$ (from Ext. Carrier Densities I)

$\quad \approx \begin{cases} \Delta n + \frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_d > N_a \\ -\frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_a > N_d \end{cases}$ (for $\Delta n \gg n_i$)

$p_v = \frac{1}{2}\left[\sqrt{\Delta n^2 + 4n_i^2} - \Delta n\right]$ (from Ext. Carrier Densities II)

$\quad \approx \begin{cases} \frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_d > N_a \\ -\Delta n - \frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_a > N_d \end{cases}$ (for $\Delta n \gg n_i$)

The p-n Junction

Informally: a p-n junction is a p-type semiconductor placed next to an n-type semiconductor.

More formally: a p-n junction is a semiconductor in which dopant concentration varies from dominantly p-type to dominantly n-type along a single spatial direction.

Coordinate System and Notation

Consider the junction of a p-type semiconductor with acceptor density N_a and n-type semiconductor with donor density N_d

Choose coordinate system so dopant concentration change along x axis and junction occurs at $x = 0$

Assumption: assume dopant densities have perfect step-function distributions of the form...

$$N_d(x) = \begin{cases} 0 & x < 0 \\ N_d & x > 0 \end{cases} \quad \text{(donor density)}$$

$$N_a(x) = \begin{cases} N_a & x < 0 \\ 0 & x > 0 \end{cases} \quad \text{(acceptor density)}$$

Condition for Semiclassical Analysis

Let $\phi(x)$ denote the electrostatic potential across the junction

Let a denote the semiconductor's lattice constant

Let E_g denote the semiconductor's band gap

Let $\Delta\phi(\Delta x)$ denote the change in potential corresponding to a distance Δx across the junction.

A necessary condition for semiclassical analysis is...

$e\Delta\phi(\Delta x) \ll E_g$ for $\Delta x \sim a$ (for semiclassical analysis)

Formation of the Depletion Region

Assume room temp. and $E_d - \mu \ll k_BT$ and $\mu - E_a \ll k_BT$

Before contact, the p-type and n-type separately obey

- n-type CB occupation is $n_c \sim N_d$

- p-type VB occupation is $p_v \sim N_a$

After contact, donor electrons in n-type region diffuse across junction to occupy acceptor holes in p-type region. Result:

- n-type region has a small layer near p-n interface of positive bound charge from positive donor ion cores

- p-type region has a small layer near p-n interface of negative bound charge from negative acceptor ion cores

- The increasing presence of positive donor cores in n-type and negative acceptor cores in p-type due to e^- diffusion establishes an internal electric field opposing further e^- diffusion from n-type to p-type.

The region of charged ion cores is called the *depletion region. There are no mobile charge carriers in the depletion region!*

$d_{pn} \sim 10\,\mathrm{nm}$ to $10^3\,\mathrm{nm}$ (typical depletion region widths)

Energy Levels Across Junction

Let $\phi(x)$ denote electrostatic potential in p-n junction

$E_c \to E_c - e_0\phi(x)$ (CB energy shifts due ϕ)

$E_v \to E_v - e_0\phi(x)$ (VB energy shifts due ϕ)

Chemical potential μ is constant across junction
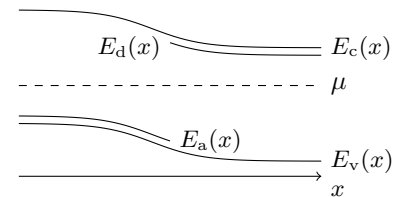
$n_c \to N_c(T)e^{-\beta(E_c - e_0\phi(x) - \mu)}$ (from shift in E_c)

$p_v \to P_v(T)e^{-\beta(\mu - E_v + e_0\phi(x))}$ (from shift in E_v)

Mathematical Analysis of the p-n Junction

This section implicitly assumes a room-temperature semiconductor obeying $E_d - \mu \ll k_BT$ and $\mu - E_a \ll k_BT$!

Goal: find potential $\phi(x)$ across the p-n junction
Concept: $\phi(x)$ varies appreciably only on a scale of the depletion region width d_{pn}, which is large on a scale of lattice constant $a \implies$ it is permissible to use *macroscopic* electrostatics equations to solve for ϕ.

$$\nabla^2\phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\epsilon\epsilon_0} \qquad \text{(Poisson equation in 3D)}$$

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{\rho(x)}{\epsilon\epsilon_0} \qquad \text{(p-n junction properties vary only with } x\text{)}$$

Boundary Conditions
Assume n-type conditions prevail for large positive x
Assume p-type conditions prevail for large negative x
$\implies n_{\mathrm{c}}(x \to \infty) = N_{\mathrm{d}}$ (all donor electrons ionized)
$\implies p_{\mathrm{v}}(x \to -\infty) = N_{\mathrm{a}}$ (all acceptor holes ionized)
Goal: relate boundary conditions to above expressions for carrier densities n_{c} and p_{v}.

<u>Conduction Band Electrons</u>
$n_{\mathrm{c}}(x) = N_{\mathrm{c}}e^{-\beta(E_{\mathrm{c}}-e_0\phi(x)-\mu)}$ (review: CB e^- density)
$n_{\mathrm{c}}(\infty) = N_{\mathrm{d}} = N_{\mathrm{c}}e^{-\beta(E_{\mathrm{c}}-e_0\phi(\infty)-\mu)}$
Divide $n_{\mathrm{c}}(x)$ by $n_{\mathrm{c}}(\infty)$ to get...
$n_{\mathrm{c}}(x) = N_{\mathrm{d}}e^{-\beta e_0(\phi(\infty)-\phi(x))}$
$\qquad\quad = N_{\mathrm{c}}e^{-\beta(E_{\mathrm{c}}-e_0\phi(x)-\mu)}$ (alternate expression)

<u>Valence Band Holes</u>
$p_{\mathrm{v}}(x) = P_{\mathrm{v}}e^{-\beta(\mu-E_{\mathrm{v}}+e_0\phi(x))}$ (review: VB hole density)
$p_{\mathrm{v}}(-\infty) = N_{\mathrm{a}} = P_{\mathrm{v}}e^{-\beta(\mu-E_{\mathrm{v}}+\phi(-\infty))}$
Divide $p_{\mathrm{v}}(x)$ by $p_{\mathrm{v}}(-\infty)$ to get...
$p_{\mathrm{v}}(x) = N_{\mathrm{a}}e^{-\beta e_0(\phi(x)-\phi(-\infty))}$
$\qquad\quad = P_{\mathrm{v}}e^{-\beta(\mu-E_{\mathrm{v}}+e_0\phi(x))}$ (alternate expression)

Relating Band Gap and Potential Drop
$n_{\mathrm{c}}(x) = N_{\mathrm{d}}e^{-\beta e_0(\phi(\infty)-\phi(x))} = N_{\mathrm{c}}e^{-\beta(E_{\mathrm{c}}-e_0\phi(x)-\mu)}$
$p_{\mathrm{v}}(x) = N_{\mathrm{a}}e^{-\beta e_0(\phi(x)-\phi(-\infty))} = P_{\mathrm{v}}e^{-\beta(\mu-E_{\mathrm{v}}+e_0\phi(x))}$
Multiply the two sides of above equations to get...
$N_{\mathrm{d}}N_{\mathrm{a}}e^{-\beta e_0(\phi(\infty)-\phi(-\infty))} = N_{\mathrm{c}}P_{\mathrm{v}}e^{-\beta(E_{\mathrm{c}}-E_{\mathrm{v}})}$
$\frac{N_{\mathrm{d}}N_{\mathrm{a}}}{N_{\mathrm{c}}P_{\mathrm{v}}} = e^{+\beta e_0(\phi(\infty)-\phi(-\infty))} \cdot e^{-\beta(E_{\mathrm{c}}-E_{\mathrm{v}})}$ (rearranged)
$\ln\frac{N_{\mathrm{d}}N_{\mathrm{a}}}{N_{\mathrm{c}}P_{\mathrm{v}}} = \beta e_0[\phi(\infty)-\phi(-\infty)] - \beta(E_{\mathrm{c}}-E_{\mathrm{v}})$ (logarithmed)
$e_0[\phi(\infty)-\phi(-\infty)] = E_{\mathrm{c}} - E_{\mathrm{v}} + k_{\mathrm{B}}T\ln\frac{N_{\mathrm{d}}N_{\mathrm{a}}}{N_{\mathrm{c}}P_{\mathrm{v}}}$ (simplified)
$e_0\Delta\phi = E_{\mathrm{g}} + k_{\mathrm{B}}T\ln\frac{N_{\mathrm{d}}N_{\mathrm{a}}}{N_{\mathrm{c}}P_{\mathrm{v}}}$ (recognizing $E_{\mathrm{g}} = E_{\mathrm{c}} - E_{\mathrm{v}}$)
$\Delta\phi = \phi(\infty) - \phi(-\infty)$ is potential drop across p-n junction
$\phi(x) - \phi(-x) \approx \Delta\phi$ for $|x| \sim 100\,\mathrm{nm}$ (in practice)

Simplified Expression for Charge Density
$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{\rho(x)}{\epsilon\epsilon_0}$ (the Poisson equation)
Solving the Poisson equation requires an expression for $\rho(x)$!
$\rho(x) = e_0[N_{\mathrm{d}}(x) - n_{\mathrm{c}}(x) - (N_{\mathrm{a}}(x) - p_{\mathrm{v}}(x))]$ (generally, assuming ionized dopant levels)

$$N_{\mathrm{d}}(x) = \begin{cases} 0 & x < 0 \\ N_{\mathrm{d}} & x > 0 \end{cases} \qquad \text{(review: assumed donor density)}$$

$$N_{\mathrm{a}}(x) = \begin{cases} N_{\mathrm{a}} & x < 0 \\ 0 & x > 0 \end{cases} \qquad \text{(review: assumed acceptor density)}$$

$n_{\mathrm{c}}(x) = N_{\mathrm{d}}e^{-\beta e_0(\phi(\infty)-\phi(x))}$ (in general; for review)
$p_{\mathrm{v}}(x) = N_{\mathrm{a}}e^{-\beta e_0(\phi(x)-\phi(-\infty))}$ (in general; for review)
Complication: the above expression for $\rho(x)$ is too complicated to analytically solve the Poisson equation.
Solution: use an approximate charge density given by...

$$\rho(x) \approx \begin{cases} 0 & x < -d_{\mathrm{p}} \\ e_0[N_{\mathrm{d}}(x) - N_{\mathrm{a}}(x)] & -d_{\mathrm{p}} < x < d_{\mathrm{n}} \\ 0 & x > d_{\mathrm{n}} \end{cases} \text{ (derived below)}$$

$n_{\mathrm{c}}p_{\mathrm{v}} = n_{\mathrm{i}}^2$ (review: law of mass action)

<u>Outside Depletion Region</u>
$\phi(x > d_{\mathrm{n}}) \sim \phi(\infty)$ (ϕ rapidly reaches asymptotic value)
$\phi(x < -d_{\mathrm{p}}) \sim \phi(-\infty)$ (ϕ rapidly reaches asymptotic value)

$n_{\mathrm{c}}(x > d_{\mathrm{n}}) \sim N_{\mathrm{d}}$ (since $\phi(x > d_{\mathrm{n}}) \sim \phi(\infty)$ in n-type)
$p_{\mathrm{v}}(x < -d_{\mathrm{p}}) \sim N_{\mathrm{a}}$ (since $\phi(x < -d_{\mathrm{p}}) \sim \phi(-\infty)$ in p-type)
$p_{\mathrm{v}}(x > d_{\mathrm{n}}) \ll n_{\mathrm{c}}(x > d_{\mathrm{n}})$ ($p_{\mathrm{v}} \sim \frac{n_{\mathrm{i}}^2}{N_{\mathrm{d}}} \ll n_{\mathrm{c}} \sim N_{\mathrm{d}}$ in n-type)
$n_{\mathrm{c}}(x < -d_{\mathrm{p}}) \ll p_{\mathrm{v}}(x < -d_{\mathrm{p}})$ ($n_{\mathrm{c}} \sim \frac{n_{\mathrm{i}}^2}{N_{\mathrm{a}}} \ll p_{\mathrm{v}} \sim N_{\mathrm{v}}$ in p-type)
$\rho(x) = e_0[N_{\mathrm{d}}(x) - n_{\mathrm{c}}(x) - (N_{\mathrm{a}}(x) - p_{\mathrm{v}}(x))]$ (generally)
$$\approx e_0\begin{cases} [0 - (N_{\mathrm{a}} - N_{\mathrm{a}})] & x < -d_{\mathrm{p}} \\ [(N_{\mathrm{d}} - N_{\mathrm{d}}) - 0] & x > d_{\mathrm{n}} \end{cases}$$
$= 0$ (outside depletion region)

<u>Inside Depletion Region</u>
$e\Delta\phi \sim E_{\mathrm{g}}$ across the depletion region $\Delta x = d_{\mathrm{n}} + d_{\mathrm{p}}$
Important: $E_{\mathrm{g}} \gg k_{\mathrm{B}}T \implies e\Delta\phi \gg k_{\mathrm{B}}T$
$n_{\mathrm{c}}(-d_{\mathrm{p}} < x < d_{\mathrm{n}}) \ll N_{\mathrm{d}}(-d_{\mathrm{p}} < x < d_{\mathrm{n}})$ (since $e\Delta\phi \gg k_{\mathrm{B}}T$)
$p_{\mathrm{v}}(-d_{\mathrm{p}} < x < d_{\mathrm{n}}) \ll N_{\mathrm{a}}(-d_{\mathrm{p}} < x < d_{\mathrm{n}})$ (since $e\Delta\phi \gg k_{\mathrm{B}}T$)
$\rho(x) = e_0[N_{\mathrm{d}}(x) - n_{\mathrm{c}}(x) - (N_{\mathrm{a}}(x) - p_{\mathrm{v}}(x))]$ (generally)
$\approx e_0[N_{\mathrm{d}}(x) - N_{\mathrm{a}}(x)]$ (inside depletion region)

<u>Result: Approximate Charge Density</u>
Combine approximate expressions for $\rho(x)$ inside and outside the depletion region to conclude that, except very near the DR boundaries $x = -d_{\mathrm{p}}$ or $x = d_{\mathrm{n}}$, $\rho(x)$ obeys...

$$\rho(x) \approx \begin{cases} 0 & x < -d_{\mathrm{p}} \\ e_0[N_{\mathrm{d}}(x) - N_{\mathrm{a}}(x)] & -d_{\mathrm{p}} < x < d_{\mathrm{n}} \\ 0 & x > d_{\mathrm{n}} \end{cases} \quad \text{(as quoted)}$$

$$= \begin{cases} 0 & x < -d_{\mathrm{p}} \\ -e_0 N_{\mathrm{a}} & -d_{\mathrm{p}} < x < 0 \\ e_0 N_{\mathrm{d}} & 0 < x < d_{\mathrm{n}} \\ 0 & x > d_{\mathrm{n}} \end{cases} \quad \text{(written in full)}$$

Solving the Poisson Equation
Goal: solve the Poisson equation for $\phi(x)$ using above $\rho(x)$
$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{\rho(x)}{\epsilon\epsilon_0}$ (Poisson equation)
$\rho(x) = [N_{\mathrm{d}}(x) - n_{\mathrm{c}}(x) - (N_{\mathrm{a}}(x) - p_{\mathrm{v}}(x))]$ (generally)

$$= \begin{cases} 0 & x < -d_{\mathrm{p}} \\ -e_0 N_{\mathrm{a}} & -d_{\mathrm{p}} < x < 0 \\ e_0 N_{\mathrm{d}} & 0 < x < d_{\mathrm{n}} \\ 0 & x > d_{\mathrm{n}} \end{cases} \quad \text{(approximately)}$$

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \begin{cases} 0 & x < -d_{\mathrm{p}} \\ \frac{e_0 N_{\mathrm{a}}}{\epsilon\epsilon_0} & -d_{\mathrm{p}} < x < 0 \\ -\frac{e_0 N_{\mathrm{d}}}{\epsilon\epsilon_0} & 0 < x < d_{\mathrm{n}} \\ 0 & x > d_{\mathrm{n}} \end{cases} \quad \text{(Poisson equation)}$$

Solving Poisson Equation: First Integration
$$\frac{\mathrm{d}\phi}{\mathrm{d}x} = \begin{cases} \phi'(-\infty) & x < -d_{\mathrm{p}} \\ \frac{e_0 N_{\mathrm{a}}}{\epsilon\epsilon_0}x + A_{\mathrm{p}} & -d_{\mathrm{p}} < x < 0 \\ -\frac{e_0 N_{\mathrm{d}}}{\epsilon\epsilon_0}x + A_{\mathrm{n}} & 0 < x < d_{\mathrm{n}} \\ \phi'(\infty) & x > d_{\mathrm{n}} \end{cases} \quad \text{(integrating } \phi''(x)\text{)}$$

<u>Boundary Conditions</u>

(i) ϕ' is continuous at $x = -d_{\mathrm{p}}$ and at $x = d_{\mathrm{n}}$

(ii) ϕ' is continuous at the p-n interface $x = 0$

(iii) ϕ' is constant for $x < -d_{\mathrm{p}}$ and $x > d_{\mathrm{n}}$

$\phi'(-d_{\mathrm{p}}^-) = 0 \equiv -\frac{e_0 N_{\mathrm{a}}}{\epsilon\epsilon_0}d_{\mathrm{p}} + A_{\mathrm{p}} = \phi'(-d_{\mathrm{p}}^+)$ (continuity at $-d_{\mathrm{p}}$)
$\implies A_{\mathrm{p}} = \frac{e_0 N_{\mathrm{a}}}{\epsilon\epsilon_0}d_{\mathrm{p}}$
$\phi'(d_{\mathrm{n}}^-) = -\frac{e_0 N_{\mathrm{d}}}{\epsilon\epsilon_0}d_{\mathrm{n}} + A_{\mathrm{n}} \equiv 0 = \phi'(d_{\mathrm{n}}^+)$ (continuity at d_{n})
$\implies A_{\mathrm{n}} = \frac{e_0 N_{\mathrm{d}}}{\epsilon\epsilon_0}d_{\mathrm{n}}$
$\phi'(-\infty) = \phi'(\infty) = 0$ (ϕ constant outside DR)

$$\implies \frac{d\phi}{dx} = \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0}(x + d_p) & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0}(x - d_n) & 0 < x < d_n \\ 0 & x > d_n \end{cases}$$

$$N_a d_p = N_d d_n \qquad \text{(from continuity at } x = 0)$$

Solving Poisson Equation: Second Integration

$$\phi(x) = \begin{cases} \phi(-\infty) & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0}\left(\frac{x^2}{2} + d_p x\right) + B_p & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0}\left(\frac{x^2}{2} - d_n x\right) + B_n & 0 < x < d_n \\ \phi(\infty) & x > d_n \end{cases} \qquad (\text{int. } \phi')$$

Boundary Conditions

(i) ϕ is continuous at the p-n interface $x = 0$

(ii) $\phi(x)$ is continuous at $x = -d_p$ and at $x = d_n$

(iii) $\phi(-\infty) \equiv 0 \implies \phi(\infty) = \Delta\phi$

$$B_p = B_n \equiv B \qquad \text{(from first BC)}$$
$$0 = -\frac{e_0 N_a}{2\epsilon\epsilon_0}d_p^2 + B \qquad \text{(continuity at } -d_p)$$
$$\implies B = \frac{e_0 N_a}{2\epsilon\epsilon_0}d_p^2 \qquad \text{(solving for } B)$$
$$\implies \phi(d_n) = \Delta\phi = \frac{e_0}{2\epsilon\epsilon_0}(N_d d_n^2 + N_a d_p^2) \qquad \text{(cont. at } d_n)$$
$$\implies B = \frac{e_0 N_a}{2\epsilon\epsilon_0}d_p^2 = \Delta\phi - \frac{e_0 N_d}{2\epsilon\epsilon_0}d_n^2 \qquad \text{(alt. expression for } B)$$

Substitute results into expression for $\phi(x)$ to get...

$$\phi(x) = \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{\epsilon\epsilon_0}\left(\frac{x^2}{2} + d_p x\right) + \frac{e_0 N_a}{2\epsilon\epsilon_0}d_p^2 & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon\epsilon_0}\left(\frac{x^2}{2} - d_n x\right) + \Delta\phi - \frac{e_0 N_d}{2\epsilon\epsilon_0}d_n^2 & 0 < x < d_n \\ \Delta\phi & x > d_n \end{cases}$$

$$= \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{2\epsilon\epsilon_0}(x + d_p)^2 & -d_p < x < 0 \\ \Delta\phi - \frac{e_0 N_d}{2\epsilon\epsilon_0}(x - d_n)^2 & 0 < x < d_n \\ \Delta\phi & x > d_n \end{cases} \qquad \text{(simplified)}$$

Depletion Region Width

Goal: determine depletion region width d_{pn} in terms of dopant densities N_a, N_d and potential difference $\Delta\phi$

$N_a d_p = N_d d_n$ (from Solving Poisson Eq. 1st Integration)

$\Delta\phi = \frac{e_0}{2\epsilon\epsilon_0}(N_d d_n^2 + N_a d_p^2)$ (from Poisson Eq. 2nd Int.)

$d_n^2 = \frac{2\epsilon\epsilon_0 \Delta\phi}{e_0(N_a + N_d)}\frac{N_a}{N_d}$ (solved for d_n)

$d_p^2 = \frac{2\epsilon\epsilon_0 \Delta\phi}{e_0(N_a + N_d)}\frac{N_d}{N_a}$ (solved for d_p)

$d_{pn} = d_n + d_p$ and some algebra leads to...

$$d_{pn} = d_n + d_p = \sqrt{\frac{2\epsilon\epsilon_0 \Delta\phi}{e_0}\frac{N_a + N_d}{N_a N_d}} \qquad \textbf{(DR width)}$$

p-n Junction with Voltage Biasing

Biasing is the application of an external bias voltage V_b across the p-n junction

Convention: V_b is positive if its application raises the potential of the p-type side relative to the n-type side.

Biasing with positive V_b is called *forward biasing*

Biasing with negative V_b is called *reverse biasing*

Let $\Delta\phi_0$ denote p-n junction potential without biasing

Let $d_{pn}^{(0)}$ denote p-n junction width without biasing

$\Delta\phi = \Delta\phi^{(0)} - V_b$ (with biasing)

Let $C \equiv \sqrt{\frac{2\epsilon\epsilon_0}{e_0}\frac{N_a + N_d}{N_a N_d}}$ (for shorthand)

$d_{pn}^{(0)} = \sqrt{C\Delta\phi_0}$ (from Depletion Region Width)

$d_{pn} = \sqrt{C\Delta\phi}$ (generalized to include biasing)

$\quad = \sqrt{C(\Delta\phi_0 - V_b)}$

$d_{pn} = d_{pn}^{(0)}\sqrt{1 - \frac{V_b}{\Delta\phi_0}}$

p-n Junction's Equilibrium $I(V)$ Characteristic

Goal: analyze dependence of electric current through junction on voltage across junction *in thermal equilibrium!*

Notation

V_b denotes external bias voltage applied to junction

$\Delta\phi = \Delta\phi_0 - V_b$ is total potential difference across junction

Let J_e denote number current density of electrons

Let J_h denote number current density of holes

Let j_e denote electric current density due to electrons

Let j_h denote electric current density due to holes

$j_e = -e_0 J_e$ (electron current densities)

$j_h = +e_0 J_h$ (hole current densities)

$J_h = J_e = 0$ (when $V_b = 0$)

Interpretation: in thermal equilibrium there is no net movement of holes or electrons across the p-n junction in the absence of an external voltage.

Components of Hole Current

The current of holes across the junction has two components...

1. *Generation current* J_h^{gen}: minority-carrier holes flowing from n-type to p-type with the p-n electric field

2. *Recombination current* J_h^{rec}: majority-carrier holes thermally excited from p-type to n-type against the p-n electric field

Hole Generation Current

- Mechanism: holes generated by thermal excitation of VB electrons at or near n-type boundary are swept across junction by p-n electric field.

- J_h^{gen} is independent of $\Delta\phi$.

Hole Recombination Current

- Mechanism: holes in p-type excited to sufficient thermal energies overcome p-n potential barrier and reach n-type, where the holes recombine with majority-carrier e^-.

- J_h^{gen} falls with $\Delta\phi$ as $J_h^{gen} \propto e^{-e_0 \beta \Delta\phi_0}$

$J_h(V_b) = J_h^{rec}(V_b) - J_h^{gen}$ (total hole current)

(assuming positive x from p-type to n-type)

Relating Hole Gen. and Recombination Currents

$J_h^{rec}(V_b) \propto e^{-\beta e_0 \Delta\phi}$ (review: hole gen. current)

$\quad = e^{-\beta e_0(\Delta\phi_0 - V_b)}$ (using $\Delta\phi = \Delta\phi_0 - V_b$)

$\quad \equiv J_0 e^{-\beta e_0(\Delta\phi_0 - V_b)}$ (defining prop. constant J_0)

$J_h^{rec}(0) = J_0 e^{-\beta e_0 \Delta\phi_0}$ (when $V_b = 0$)

Review: $J_h = 0$ in thermal equilibrium when $V_b = 0$

$\implies J_h^{gen} = J_h^{rec}(V_b)\big|_{V_b=0} = J_0 e^{-\beta e_0 \Delta\phi_0}$

Divide $J_h^{rec}(V_b)$ by $J_h^{gen} = J_0 e^{-\beta e_0 \Delta\phi_0}$ and rearrange to get...

$J_h^{rec}(V_b) = J_h^{gen} e^{+\beta e_0 V_b}$ (hole recombination current)

$J_h(V_b) = J_h^{rec}(V_b) - J_h^{gen}$ (total hole current)

$\quad = J_h^{gen}(e^{\beta e_0 V_b} - 1)$ **(total hole current)**

Components of Electron Current

The current of e^- across the junction has two components...

1. *Generation current* J_e^{gen}: minority-carrier electrons flowing from p-type to n-type with the p-n electric field.

2. *Recombination current* J_e^{rec}: majority-carrier electrons flowing from n-type to p-type with the p-n electric field.

Electron Generation Current

- Mechanism: electrons drifting to edge p-type boundary are swept across junction by p-n electric field.

- $J_{\mathrm{e}}^{\mathrm{gen}}$ is independent of $\Delta\phi$

<u>Electron Recombination Current</u>

- Mechanism: e^- in n-type excited to sufficient thermal energies overcome p-n potential barrier and reach p-type

- $J_{\mathrm{e}}^{\mathrm{rec}}$ falls with $\Delta\phi$ as $J_{\mathrm{e}}^{\mathrm{gen}} \propto e^{-e_0\beta\Delta\phi}$

$$J_{\mathrm{e}}(V_{\mathrm{b}}) = J_{\mathrm{e}}^{\mathrm{gen}} - J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}}) \qquad \text{(total electron current)}$$

Relating Electron Gen. and Recombination Currents

$$\begin{aligned}
J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}}) &\propto e^{-\beta e_0 \Delta\phi} && \text{(review: electron gen. current)}\\
&= e^{-\beta e_0(\Delta\phi_0 - V_{\mathrm{b}})} && \text{(using } \Delta\phi = \Delta\phi_0 - V_{\mathrm{b}})\\
J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}}) &\equiv J_0 e^{-\beta e_0(\Delta\phi_0 - V_{\mathrm{b}})} && \text{(defining prop. constant)}\\
J_{\mathrm{e}}^{\mathrm{rec}}(0) &= J_0 e^{-\beta e_0 \Delta\phi_0} && \text{(when } V_{\mathrm{b}} = 0)
\end{aligned}$$

Review: $J_{\mathrm{e}} = 0$ in thermal equilibrium when $V_{\mathrm{b}} = 0$

$$\implies J_{\mathrm{e}}^{\mathrm{gen}} = J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}})\big|_{V_{\mathrm{b}}=0} = J_0 e^{-\beta e_0 \Delta\phi_0}$$

Divide $J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}})$ by $J_{\mathrm{e}}^{\mathrm{gen}} = J_0 e^{-\beta e_0 \Delta\phi_0}$ and rearrange to get...

$$\begin{aligned}
J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}}) &= J_{\mathrm{e}}^{\mathrm{gen}} e^{+\beta e_0 V_{\mathrm{b}}} && \text{(electron recombination current)}\\
J_{\mathrm{e}}(V_{\mathrm{b}}) &= J_{\mathrm{e}}^{\mathrm{gen}} - J_{\mathrm{e}}^{\mathrm{rec}}(V_{\mathrm{b}}) && \text{(total electron current)}\\
&= -J_{\mathrm{e}}^{\mathrm{gen}}(e^{\beta e_0 V_{\mathrm{b}}} - 1) && \textbf{(total electron current)}
\end{aligned}$$

Total Electric Current Across Junction

$$\begin{aligned}
j_{\mathrm{h}} &= +e_0 J_{\mathrm{h}}\\
&= e_0 J_{\mathrm{h}}^{\mathrm{gen}}(e^{\beta e_0 V_{\mathrm{b}}} - 1)\\
j_{\mathrm{e}} &= -e_0 J_{\mathrm{e}}\\
&= e_0 J_{\mathrm{e}}^{\mathrm{gen}}(e^{\beta e_0 V_{\mathrm{b}}} - 1)\\
j_{\mathrm{tot}} &= j_{\mathrm{e}} + j_{\mathrm{h}} && \textbf{(total electric current)}\\
&= e_0 \left(J_{\mathrm{h}}^{\mathrm{gen}} + J_{\mathrm{e}}^{\mathrm{gen}}\right) \cdot \left(e^{\beta e_0 V_{\mathrm{b}}} - 1\right)
\end{aligned}$$

Lattice Oscillations

Motivation: in practice, the ions forming a crystal are not rigidly fixed, but may oscillate about their equilibrium positions.

Classical Theory of Lattice Oscillations

General idea: model oscillating crystal lattice as a system of harmonic oscillators using classical mechanics.

One-Dimensional, Monoatomic Lattice

Consider a one-dimensional monoatomic lattice with lattice constant a formed of N ions with mass M.
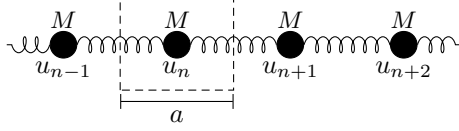
Notation for Ion Position

$R_n^{(0)} = na, \; n \in \mathbb{Z}$ (equilibrium position of n-th ion)

Let u_n denote displacement from equilibrium of ion at $R = na$

$R_n(t) = R_n^{(0)} + u_n(t)$ (instantaneous position of n-th ion)

$\langle u_n(t) \rangle = 0$ (average position is equilibrium position)

$\implies \langle R_n(t) \rangle = R_n^{(0)}$ (average position is equilibrium)

Equations of Motion

Assume ions interact only with their nearest neighbors!

Plan: expand lattice's potential energy U to second order in ion displacement u_n from equilibrium position.

- Choose global potential level so equilibrium pot. is zero
- First-order term vanishes, since $\frac{\partial U}{\partial x} = 0$ in equilibrium
- Model second-order term with a harmonic potential of the form $U_n = \frac{K}{2}(u_n - u_{n+1})^2$

$U = \frac{K}{2} \sum_n (u_n - u_{n+1})^2 + \mathcal{O}(u_n^3)$ (lattice potential energy)

$F_n = -\frac{\partial U}{\partial u_n}$ (force on n-th ion)

$= -K(u_n - u_{n+1}) + K(u_{n-1} - u_n)$ (from above U)

$= -K(2u_n - u_{n+1} - u_{n-1})$ (simplified)

$M\ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1})$ (Newton's law for n-th ion)

Interpretation: the equation of motion is the same as for a chain of point masses M connected by identical ideal springs of spring constant K.

Solution and Dispersion Relation

$M\ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1})$ (Newton's law for n-th ion)

$u_n(t) = u_0 e^{i(kna - \omega t)}$ (ansatz for solutions)

Substitute ansatz into Newton's law and to get...

$-M\omega^2 u_0 e^{i(\omega t - kna)} = -K u_0 e^{i(kna - \omega t)}(2 - e^{ika} - e^{-ika})$

$M\omega^2 = 2K(1 - \cos ka)$ (simplifying)

$= 4K \sin^2 \frac{ka}{2}$ (using $1 - \cos x = 2\sin^2 \frac{x}{2}$)

$\omega = 2\sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right|$ (dispersion relation)

Boundary Conditions

Assume periodic boundary conditions of the form $u_{N+1} = u_1$

Rationale: this analysis considers only bulk crystal properties, so if N is large (and thus surface effects are immaterial) we may choose analytically convenient periodic BC.

$u_{N+1} \equiv u_1$ (assume periodic BC)

$u_n = u_0 e^{i(kna - \omega t)}$ (review: displacement of n-th ion)

$\implies e^{ik(N+1)a} \equiv e^{ika}$ (using $u_{N+1} \equiv u_1$)

$\implies e^{ikNa} = 1$ (simplifying)

$\implies kNa = 2\pi m, \; m \in \mathbb{Z}$

$\implies k = \frac{2\pi}{Na} m$

Result: PBC require that k is discretized into N values

Convention: choose m such that...

$m \in \begin{cases} -\frac{N}{2}, \ldots, \frac{N}{2} & N \text{ even} \\ -\frac{N-1}{2}, \ldots, \frac{N+1}{2} & N \text{ odd} \end{cases}$

$\implies k \in \left(-\frac{\pi}{a}, \frac{\pi}{a} \right]$ (k is restricted to first BZ)

Analyzing Solution

$u_n(t) = u_0 e^{i(kna - \omega t)}$ (review: ion displacement)

$\omega(k) = 2\sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right|$ (review: dispersion relation)

Special case: $k = 0$

$\omega(0) = 0$ (when $k = 0$)

$u_n(t) = u_0$ (when $k = 0$)

Interpretation: $u_n(t) = u_0$ for all n represents a translation of the entire lattice.

Special case: $k = \pi/a$

$\omega(\pi/a) = 2\sqrt{\frac{K}{M}}$ (when $k = \pi/2$)

$u_n = u_0 e^{i\pi n} e^{-i\sqrt{\frac{K}{M}} t}$ (when $k = \pi/2$)

$= u_0 (-1)^n e^{-i\sqrt{\frac{K}{M}} t}$ (when $k = \pi/2$)

Interpretation: this solution represents neighboring ions compressing/expanding in phase with equal amplitude.

Analyzing Dispersion Relation

$\omega(k) = 2\sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right|$ (review: dispersion relation)

$\approx \sqrt{\frac{K}{M}} ka$ (for $ka \ll 1$)

$c = \frac{\omega}{k}$ (phase velocity)

$\approx \sqrt{\frac{K}{M}} a$ (for $ka \ll 1$)

$v_g = \frac{\partial \omega}{\partial k} = a\sqrt{\frac{K}{M}} \cos\left(\frac{ka}{2} \right)$

Interpretation: group velocity is the velocity at which a local disturbance, described by a wave packet, would propagate through the lattice chain

$\psi_k(n) = \sum_k A(k) u_0 e^{i(kna - \omega(k)t)}$ (wave packet ansatz)

$A(k)$ is an amplitude function used to center wave packet about a given k

$v_g(\pi/a) = 0$ (disturbances at $k = \frac{\pi}{a}$ cause standing waves)

1D Lattice with a Diatomic Basis

Consider a one-dimensional lattice of lattice constant a with two ions per primitive cell, one with mass M at the lattice site and one with mass m a distance d form the lattice site.
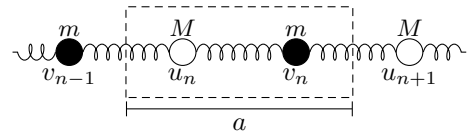
Notation

$R_{n_j}^{(0)} = na + d_j, \; n \in \mathbb{Z}$ (equilibrium positions of ions)

$d_j = \begin{cases} 0 & \text{for ion } M \\ d & \text{for ion } m \end{cases}$ (two-ion basis)

u_n is displacement from equilibrium of ion M

v_n is displacement from equilibrium of ion m

Equations of Motion

Assumptions:

(i) ions interact only with their nearest neighbors

(ii) all interactions are modeled by same spring constant K

$U = \frac{K}{2} \sum_n \left[(u_n - v_n)^2 + (v_n - u_{n+1})^2 \right]$ (lattice potential)

$F_{u_n} = -\frac{\partial U}{\partial u_n}$ (force on M ions)

$= -K(u_n - v_n) - K(u_n - v_{n-1})$

$$= -K(2u_n - v_n - v_{n-1})$$
$$F_{v_n} = -\frac{\partial U}{\partial v_n} \qquad \text{(force on } m \text{ ions)}$$
$$= K(u_n - v_n) + K(u_{n+1} - v_n)$$
$$= -K(2v_n - u_n - u_{n+1})$$
$$M\ddot{u}_n = -K(2u_n - v_n - v_{n-1}) \qquad \text{(Newton's law for } u_n \text{ ion)}$$
$$M\ddot{v}_n = -K(2v_n - u_n - u_{n+1}) \qquad \text{(Newton's law for } v_n \text{ ion)}$$

Solution and Dispersion Relation

$$M\ddot{u}_n = -K(2u_n - v_n - v_{n-1}) \qquad \text{(Newton's law for } u_n \text{ ion)}$$
$$m\ddot{v}_n = -K(2v_n - u_n - u_{n+1}) \qquad \text{(Newton's law for } v_n \text{ ion)}$$
$$u_n(t) = u_0 e^{i(kna - \omega t)} \qquad \text{(ansatz for solutions)}$$
$$v_n(t) = v_0 e^{i(kna - \omega t)} \qquad \text{(ansatz for solutions)}$$

Substitute ansatzes into equations of motion to get...
$$M\omega^2 u_0 = K(2u_0 - v_0 - v_0 e^{-ika})$$
$$m\omega^2 v_0 = K(2v_0 - u_0 - u_0 e^{+ika})$$

Write the homogeneous system of eqs. in matrix form to get...
$$\begin{pmatrix} M\omega^2 - 2K & K(1 + e^{-ika}) \\ K(1 + e^{+ika}) & m\omega^2 - 2K \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0} \qquad \text{(matrix form)}$$

For a nontrivial solution for u_0 and v_0, require...
$$0 \equiv \det \begin{pmatrix} M\omega^2 - 2K & K(1 + e^{-ika}) \\ K(1 + e^{+ika}) & m\omega^2 - 2K \end{pmatrix}$$
$$= Mm\omega^4 - 2K(M+m)\omega^2 + 4K^2 - 2K^2(1 + \cos ka)$$
$$= Mm\omega^4 - 2K(M+m)\omega^2 - 4K^2 \sin^2 \tfrac{ka}{2}$$

Apply the quadratic formula to get the dispersion relation...
$$\omega_\pm^2 = K\left(\frac{1}{m} + \frac{1}{M} \pm \sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4}{mM}\sin^2 \tfrac{ka}{2}} \right)$$
$$= K\frac{m+M}{mM}\left[1 \pm \sqrt{1 - \frac{4mM}{m+M}\sin^2 \tfrac{ka}{2}} \right]$$

Dispersion Relation: Acoustic Branch as k → 0

First consider the acoustic branch ω_- as $k \to 0$
$$\omega_-^2 = K\frac{m+M}{mM}\left[1 - \sqrt{1 - \frac{4mM}{m+M}\sin^2 \tfrac{ka}{2}} \right] \qquad \text{(in general)}$$
$$\to K\frac{m+M}{mM}\left[1 - \left(1 - \frac{2mM}{(m+M)^2}\sin^2 \tfrac{ka}{2}\right) \right] \quad \left(\sqrt{1-x} \approx 1 - \tfrac{x}{2}\right)$$
$$= \frac{2K}{m+M}\sin^2 \tfrac{ka}{2}$$
$$\omega_- = +\sqrt{\frac{2K}{m+M}}\sin \tfrac{ka}{2} \qquad \text{(take + sqrt. on physical grounds)}$$
$$\approx \sqrt{\frac{K}{2(m+M)}}ka \qquad \text{(using } \sin x = x + \mathcal{O}(x^3))$$
$$c_- = \frac{\omega_-}{k} = \sqrt{\frac{K}{2(m+M)}}a \qquad \text{(constant phase velocity as } k \to 0)$$

Motion: in a given primitive cell, m and M oscillate in phase, and the motion of all cells is identical.

Dispersion Relation: Optical Branch as k → 0

Next consider the optical branch ω_+ as $k \to 0$
$$\omega_+^2 = K\frac{m+M}{mM}\left[1 + \sqrt{1 - \frac{4mM}{m+M}\sin^2 \tfrac{ka}{2}} \right] \qquad \text{(in general)}$$
$$\to 2K\frac{m+M}{mM} \qquad \text{(as } k \to 0) \qquad \omega_+ = \sqrt{2K\frac{m+M}{mM}}$$

Motion: in a given primitive cell, m and M ions oscillate in anti-phase, and the motion of all cells is identical.

Dispersion Relation: Limit as k → π/a

$$\omega_\pm^2 = K\left[\frac{m+M}{mM} \pm \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{mM}\sin^2 \tfrac{ka}{2}} \right] \qquad \text{(in general)}$$
$$\to K\left[\frac{m+M}{mM} \pm \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{mM}} \right] \qquad \text{(as } k \to \tfrac{\pi}{a})$$
$$= K\left[\frac{m+M}{mM} \pm \sqrt{\left(\frac{1}{m} - \frac{1}{M}\right)^2} \right] \qquad \text{(assuming } M > m)$$
$$= \begin{cases} \frac{2K}{m} & \text{for } \omega_+ \\ \frac{2K}{M} & \text{for } \omega_- \end{cases}$$

Motion: for $\omega_+ = \sqrt{\frac{2K}{m}}$, the M ions are at rest and m ions oscillate in anti-phase pairs across neighboring cells.

Motion: for $\omega_- = \sqrt{\frac{2K}{M}}$, the m ions are at rest and M ions oscillate in anti-phase pairs across neighboring cells.

Quantum Theory of Lattice Oscillations

Goal: replace the above classical discussion of lattice oscillations to a quantum-mechanical treatment.

One-Dimensional, Monoatomic Lattice

Consider a one-dimensional monoatomic lattice of N ions of mass M and lattice constant a, indexed by $n \in \mathbb{Z}$.
Consider only interactions between nearest-neighbor ions
Let K denote the harmonic interaction spring constant
Let u and p denote position and momentum operators

General Considerations

$$H = \sum_n \frac{p_n^2}{2M} + \frac{K}{2}(u_n - u_{n+1})^2 \qquad \text{(lattice Hamiltonian)}$$
Assume periodic boundary conditions of the form...
$$u_{N+1} = u_1 \qquad \text{(assume periodic BC)}$$
$$p_{N+1} = p_1 \qquad \text{(assume periodic BC)}$$

Fourier Expansions of Position and Momentum

Plan: expand operators as Fourier series of the form...
$$u_n = \frac{1}{\sqrt{N}}\sum_k Q_k e^{ikna} \qquad \text{(Fourier expansion of } u_n)$$
$$Q_k = \frac{1}{\sqrt{N}}\sum_n u_n e^{-ikna} \qquad \text{(Fourier coefficients for } u_n)$$
$$p_n = \frac{1}{\sqrt{N}}\sum_k P_k e^{ikna} \qquad \text{(Fourier expansion of } p_n)$$
$$P_k = \frac{1}{\sqrt{N}}\sum_n p_n e^{-ikna} \qquad \text{(Fourier coefficients for } p_n)$$
$$k = \frac{2\pi}{Na}m \text{ where } m = 0, \pm 1, \ldots, \pm\left(\frac{N}{2} - 1\right), \frac{N}{2} \qquad \text{(from BPC)}$$

Commutation Relations

$[u_n, p_m] = i\hbar\delta_{nm}$ (review: canonical commutation relation)
Interpretation: operators associated with different ions commute
Goal: use $[u_n, p_m] = i\hbar\delta_{nm}$ to find show $[Q_k, P_{k'}] = i\hbar\delta_{kk'}$.
$$[Q_k, P_{k'}] = \frac{1}{N}\sum_{n,n'}[u_n, p_{n'}]e^{i(k'n' - kn)a} \qquad \text{(from above } u_n, p_n)$$
$$= \frac{i\hbar}{N}\sum_{n,n'}\delta_{nn'}e^{i(k'n' - kn)a} \qquad \text{(using } [u_n, p_{n'}] = i\hbar\delta_{nn'})$$
$$= \frac{i\hbar}{N}\sum_n e^{i(k'-k)na} \qquad \text{(using Kronecker delta } \delta_{nn'})$$
$$= \frac{i\hbar}{N}\sum_n e^{i\frac{2\pi}{N}(m'-m)n} \qquad \text{(using } k = \frac{2\pi m}{Na})$$
$$= \frac{i\hbar}{N}\sum_{n=0}^{N-1} e^{i\frac{2\pi}{N}\ell n} \qquad \text{(letting } \ell \equiv m' - m)$$
$$= \frac{i\hbar}{N}\frac{1 - e^{2\pi i\ell}}{1 - e^{i\frac{2\pi}{N}\ell}} \qquad \text{(summing geometric series)}$$
$$= \frac{i\hbar}{N}\begin{cases} N & \ell = 0 \\ 0 & \ell \in \mathbb{Z} \setminus \{0\} \end{cases} \qquad \text{(L'Hôpital's rule for 0/0)}$$
$$= i\hbar\delta_{\ell,0} = i\hbar\delta_{m,m'} = i\hbar\delta_{k,k'}$$
$$[Q_k, P_{k'}] = i\hbar\delta_{k,k'} \qquad \text{(result: commutator } [Q_k, P_{k'}])$$

Hamiltonian in Terms of P_k and Q_k

$$H = \sum_n \frac{p_n^2}{2M} + \frac{K}{2}(u_n - u_{n+1})^2 \qquad \text{(in terms of } u_n \text{ and } p_n)$$
$$\frac{1}{N}\sum_n e^{i(k'-k)na} = \delta_{k,k'} \qquad \text{(identity from above for reference)}$$
$$H_{\text{kin}} = \sum_n \frac{p_n^2}{2M} = \frac{1}{2MN}\sum_{n,k,k'} P_k P_{k'} e^{i(k+k')na} \qquad \text{(kinetic term)}$$
$$= \frac{1}{2M}\sum_{k,k'} P_k P_{k'}\delta_{k,-k'} \qquad \text{(see identity above)}$$
$$= \frac{1}{2M}\sum_k P_k P_{-k} \qquad \text{(using Kronecker delta } \delta_{k,-k'})$$
$$H_{\text{pot}} = \sum_n \frac{K}{2}(u_n - u_{n+1})^2 \qquad \text{(potential term)}$$
$$= \frac{K}{2N}\sum_{n,k,k'} Q_k Q_{k'}\left(e^{ikna} - e^{ik(n+1)a}\right)\left(e^{ik'na} - e^{ik'(n+1)a}\right)$$
$$= \frac{K}{2N}\sum_{n,k,k'} Q_k Q_{k'}\left(1 - e^{ika}\right)\left(1 - e^{ik'a}\right)e^{i(k+k')na}$$
$$= \frac{K}{2}\sum_{k,k'} Q_k Q_{k'}\left(1 - e^{ika}\right)\left(1 - e^{ik'a}\right)\delta_{k,-k'} \quad \text{(identify above)}$$
$$= \frac{K}{2}\sum_k Q_k Q_{-k}\left(1 - e^{ika}\right)\left(1 - e^{-ika}\right) \qquad \text{(using } \delta_{k,-k'})$$
$$= \frac{K}{2}\sum_k Q_k Q_{-k}(2 - 2\cos ka) \qquad \text{(exponential to sinusoid)}$$

$$= K \sum_k Q_k Q_{-k}(1 - \cos ka) \qquad \text{(simplifying)}$$

Let $K(1 - \cos ka) \equiv \frac{1}{2}M\omega_k^2$ $\qquad$ (defining frequency ω_k)

$$\omega_k = \sqrt{\frac{2K}{M}(1 - \cos ka)} \qquad \text{(solving for } \omega_k)$$

$$= \sqrt{\frac{2K}{M} \cdot 2\sin^2 \frac{ka}{2}} \qquad \text{(using } 1 - \cos x = 2\sin^2 \frac{x}{2})$$

$$= 2\sqrt{\frac{K}{M}}\left|\sin \frac{ka}{2}\right| \qquad \text{(simplifying)}$$

$$H_{\text{pot}} = \frac{M}{2}\sum_k \omega_k^2 Q_k Q_{-k} \qquad \text{(in terms of } \omega_k)$$

Combine kinetic and potential Hamiltonian terms to get...

$$H = H_{\text{kin}} + H_{\text{pot}} \qquad \text{(Hamiltonian in terms of } P_k \text{ and } Q_k)$$

$$= \sum_k \left[\frac{P_k P_{-k}}{2M} + K(1 - \cos ka)Q_k Q_{-k} \right]$$

$$= \sum_k \left(\frac{P_k P_{-k}}{2M} + \frac{M\omega_k^2}{2}Q_k Q_{-k} \right) \qquad \text{(in terms of } \omega_k)$$

Review: Miscellaneous Quantum Mechanics

The time evolution of an operator O in a system governed by the Hamiltonian H is...

$$i\hbar \frac{dO}{dt} = [Q, H] \qquad \text{(time evolution of } O)$$

$$[A, BC] = B[A, C] + [A, B]C \qquad \text{(commutator property)}$$

Review: Quantum Harmonic Oscillator

Consider a QHO of mass m and frequency ω.

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{i}{m\omega}p\right) \qquad \text{(lowering operator)}$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{i}{m\omega}p\right) \qquad \text{(raising operator)}$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(a^\dagger + a\right) \qquad (x \text{ in terms of } a \text{ and } a^\dagger)$$

$$p = i\sqrt{\frac{\hbar m\omega}{2}}\left(a^\dagger - a\right) \qquad (p \text{ in terms of } a \text{ and } a^\dagger)$$

$$H_{\text{QHO}} = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 \qquad \text{(QHO's Hamiltonian)}$$

$$= \hbar\omega\left(\frac{1}{2} + a^\dagger a\right) \qquad \text{(in terms of } a \text{ and } a^\dagger)$$

$$[a, a^\dagger] = 1 \qquad \text{(commutation relation)}$$

Let $|n\rangle$ where $n = 0, 1, \ldots$ denote n-th QHO eigenstate

$$a|n\rangle = \sqrt{n}\,|n-1\rangle \qquad \text{(action of lowering operator)}$$

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle \qquad \text{(action of raising operator)}$$

$$a^\dagger a|n\rangle = n|n\rangle \qquad (a^\dagger a \text{ is ``counting'' operator)}$$

Hamiltonian as Sum of Uncoupled Oscillators

Goal: show above Hamiltonian is a sum of Hamiltonians of uncoupled (independent) harmonic oscillators.

Plan:

1. find time evolutions of $\dot{Q}_k$ and $\ddot{Q}_k$ and match to harmonic oscillator form $\ddot{Q} + \omega^2 Q = 0$

2. write Hamiltonian in terms of ladder operators a^+ and a and match to QHO Hamiltonian $H = \hbar\omega\left(\frac{1}{2} + a^\dagger a\right)$

First Time Evolution of Q_k

$$i\hbar\dot{Q}_k = [Q_k, H] \qquad \text{(by definition)}$$

$$= [Q_k, H_{\text{kin}} + H_{\text{pot}}] \qquad \text{(decomposing Hamiltonian)}$$

$$= [Q_k, H_{\text{kin}}] \qquad (Q_k \text{ commutes with all } Q_{k'} \text{ in } H_{\text{pot}})$$

$$= \left[Q_k, \frac{1}{2M}\sum_{k'} P_{k'}P_{-k'}\right] \qquad \text{(from expression for } H_{\text{kin}})$$

$$= \frac{1}{2M}\sum_{k'} P_{k'}[Q_k, P_{-k'}] + [Q_k, P_{k'}]P_{-k'} \qquad \text{(comm. prop.)}$$

$$= \frac{i\hbar}{2M}\sum_{k'} P_{k'}\delta_{k,-k'} + \delta_{k,k'}P_{-k'} \qquad ([Q_k, P_{k'}] = i\hbar\delta_{kk'})$$

$$= 2\frac{i\hbar}{2M}P_{-k} \qquad \text{(using Kronecker deltas)}$$

$$\implies \dot{Q}_k = \frac{1}{M}P_{-k} \qquad \text{(result: time evolution of } Q_k)$$

Second Time Evolution of Q_k

$$i\hbar\ddot{Q}_k = [\dot{Q}_k, H] \qquad \text{(by definition)}$$

$$= \frac{1}{M}[P_{-k}, H_{\text{pot}} + H_{\text{kin}}] \qquad \text{(from above } \dot{Q}_k)$$

$$= \frac{1}{M}[P_{-k}, H_{\text{pot}}] \qquad (P_{-k} \text{ commutes with all } P_k \text{ in } H_{\text{kin}})$$

$$= \frac{1}{M}\left[P_{-k}, \frac{M}{2}\sum_{k'}\omega_{k'}^2 Q_{k'}Q_{-k'}\right] \qquad \text{(from above } H_{\text{pot}})$$

$$= \frac{1}{2}\sum_{k'}\omega_{k'}^2\left(Q_{k'}[P_{-k}, Q_{-k'}] + [P_{-k}, Q_{k'}]Q_{-k'}\right)$$

$$= -\frac{i\hbar}{2}\sum_{k'}\omega_{k'}^2\left(Q_{k'}\delta_{-k,-k'} + \delta_{-k,k'}Q_{-k'}\right)$$

(using $[P_k, Q_{k'}] = -i\hbar\delta_{k,k'}$)

$$= -\frac{i\hbar}{2}\omega_k^2\left(Q_k + Q_k\right)$$

$$\implies \ddot{Q}_k = -\omega_k^2 Q_k \qquad \text{(result: time evolution of } \dot{Q}_k)$$

Rearrange to get...

$$\ddot{Q}_k + \omega_k^2 Q_k = 0 \qquad \text{(equation for harmonic oscillator)}$$

Hamiltonian in Terms of Ladder Operators

$$H = \sum_k \left(\frac{P_k P_{-k}}{2M} + \frac{M\omega_k^2}{2}Q_k Q_{-k} \right) \qquad \text{(review: lattice Ham.)}$$

$$Q_k = \sqrt{\frac{\hbar}{2M\omega_k}}\left(a_k + a_{-k}^\dagger\right) \qquad \text{(quoted)}$$

$$P_k = i\sqrt{\frac{\hbar M\omega_k}{2}}\left(a_k^\dagger - a_{-k}\right) \qquad \text{(quoted)}$$

Justification: these definitions of Q_k and P_k preserve the commutation relation $[Q_k, P_{k'}] = i\hbar\delta_{k,k'}$ via $[a, a^\dagger] = 1$.

$$[Q_k, P_{k'}] = \frac{i\hbar}{2}\left[(a_k + a_{-k}^\dagger), (a_{k'}^\dagger - a_{-k'})\right] \qquad \text{(proving com. rel.)}$$

$$= \frac{i\hbar}{2}\left([a_k, a_{k'}^\dagger] - [a_k, a_{-k'}] + [a_{-k}^\dagger, a_{k'}^\dagger] - [a_{-k}^\dagger, a_{-k'}]\right)$$

$$= \frac{i\hbar}{2}\left([a_k, a_{k'}^\dagger] - [a_{-k}^\dagger, a_{-k'}]\right) \qquad ([a, a] = [a^\dagger, a^\dagger] = 0)$$

$$= i\hbar\delta_{kk'} \qquad \text{(using } [a_k, a_k^\dagger] = \delta_{kk'})$$

Substitute Q_k and P_k into lattice Hamiltonian to get...

$$H = \sum_k \left(\frac{P_k P_{-k}}{2M} + \frac{M\omega_k^2}{2}Q_k Q_{-k} \right) \qquad \text{(review: lattice Ham.)}$$

$$= -\frac{1}{2M}\frac{\hbar M}{2}\sum_k \omega_k(a_k^\dagger - a_{-k})(a_{-k}^\dagger - a_k)$$

$$+ \frac{M}{2}\frac{\hbar}{2M}\sum_k \frac{\omega_k}{\omega_k}(a_k + a_{-k}^\dagger)(a_{-k} + a_k^\dagger)$$

$$= \frac{\hbar}{4}\sum_k \omega_k\left[(a_k + a_{-k}^\dagger)(a_{-k} + a_k^\dagger) - (a_k^\dagger - a_{-k})(a_{-k}^\dagger - a_k)\right]$$

$$[a_k, a_{k'}] = 0 \implies a_k a_{k'} = a_{k'}a_k \; \forall \, k, k' \qquad \text{(for simplifying)}$$

$$[a_k^\dagger, a_{k'}^\dagger] = 0 \implies a_k^\dagger a_{k'}^\dagger = a_{k'}^\dagger a_k^\dagger \; \forall \, k, k' \qquad \text{(for simplifying)}$$

Multiply out Hamiltonian and simplify to get...

$$H = \frac{\hbar}{4}\sum_k \omega_k\left(a_k^\dagger a_k + a_{-k}a_{-k}^\dagger + a_{-k}^\dagger a_{-k} + a_k a_k^\dagger\right)$$

$$= \frac{\hbar}{4}\sum_k \omega_k\left(2a_k^\dagger a_k + 2a_k a_k^\dagger\right) \qquad \text{(using } a_k = a_{-k}^\dagger)$$

$$= \sum_k \hbar\omega_k\left(a_k^\dagger a_k + \frac{1}{2}\right) \qquad \text{(using } a_k a_k^\dagger = 1 + a_k^\dagger a_k)$$

$$= \sum_k H_{\text{QHO}}^{(k)} \qquad \text{(result: sum of independent QHO)}$$

Internal Energy and Heat Capacity

Goal: develop expressions for phonon contributions to a 3D lattice's internal energy and heat capacity

Review: Statistical Physics

Consider a system of volume V with discrete energy states $\{E_i\}$

$$Z_c = \sum_i e^{-\beta E_i} \qquad \text{(canonical partition function)}$$

$$u = \frac{1}{VZ_c}\sum_i E_i e^{-\beta E_i} \qquad \text{(system's specific internal energy)}$$

$$f = \frac{1}{V}\ln Z_c \qquad \text{(defining the quantity } f)$$

$$= \frac{1}{V}\ln\left(\sum_i e^{-\beta E_i}\right) \qquad \text{(substituting in } Z_c)$$

$$u = -\frac{\partial f}{\partial \beta} \qquad \text{(internal energy in terms of } f)$$

$$c_V = \frac{\partial u}{\partial T} \qquad \text{(specific heat capacity)}$$

Lattice's Internal Energy

Without derivation, a harmonic 3D lattice's total energy is...

$$E = \sum_{\mathbf{k}s}\left(n_{\mathbf{k}s} + \frac{1}{2}\right)\hbar\omega_s(\mathbf{k}) \qquad \text{(lattice energy)}$$

Heuristic justification: A harmonic lattice's Hamiltonian may be decomposed into a sum of uncoupled quantum harmonic oscillators $\implies$ the total lattice energy should equal the sum of the energies of the individual QHO.

$$Z_c = \sum_i e^{\beta E_i} = \prod_{\mathbf{k}s}\left[\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_s(\mathbf{k})\left(n+\frac{1}{2}\right)}\right] \qquad \text{(lattice's part. func.)}$$

$$= \prod_{\mathbf{k}s} e^{-\beta\hbar\omega_s(\mathbf{k})/2}\left[\sum_{n=0}^{\infty}\left(e^{-\beta\hbar\omega_s(\mathbf{k})}\right)^n\right]$$

$$= \prod_{\mathbf{k}s}\frac{e^{-\beta\hbar\omega_s(\mathbf{k})/2}}{1 - e^{-\beta\hbar\omega_s(\mathbf{k})}} \qquad \text{(summing the geometric series)}$$

$$= \prod_{\mathbf{k}s} \frac{e^{-\beta\hbar\omega_s(\mathbf{k})/2}}{1-e^{-\beta\hbar\omega_s(\mathbf{k})}} \qquad \text{(summing the geometric series)}$$

$$f = \frac{1}{V}\ln Z_c = \frac{1}{V}\ln \prod_{\mathbf{k}s} \frac{e^{-\beta\hbar\omega_s(\mathbf{k})/2}}{1-e^{-\beta\hbar\omega_s(\mathbf{k})}} \qquad \text{(lattice's value of } f\text{)}$$

$$= \frac{1}{V}\sum_{\mathbf{k}s} \ln \frac{e^{-\beta\hbar\omega_s(\mathbf{k})/2}}{1-e^{-\beta\hbar\omega_s(\mathbf{k})}} \qquad \text{(using } \ln ab = \ln a + \ln b\text{)}$$

$$u = -\frac{\partial f}{\partial \beta} \qquad \text{(in general)}$$

$$= \frac{1}{V}\sum_{\mathbf{k}s} \left(\frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} + \frac{1}{2} \right)\hbar\omega_s(\mathbf{k}) \qquad \textbf{(lattice internal energy)}$$

Average Normal Mode Excitation Number

$$u = \frac{1}{V}\sum_{\mathbf{k}s} \left(\frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} + \frac{1}{2} \right)\hbar\omega_s(\mathbf{k}) \qquad \text{(review: internal energy)}$$

$$E = \sum_{\mathbf{k}s} \left(n_{\mathbf{k}s} + \frac{1}{2} \right)\hbar\omega_s(\mathbf{k}) \qquad \text{(review: total energy)}$$

Recall u is (implicitly) the lattice's *average* internal energy
Compare expressions for E and u to conclude...

$$n_s(\mathbf{k}) = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} \qquad \text{(mean excitation number)}$$

Interpretation: $n_s(\mathbf{k})$ is the mean excitation number of the $(\mathbf{k}, s)$ lattice normal mode at temperature $T = 1/k_B T$.
Equivalently: $n_s(\mathbf{k})$ is the mean number of phonons with index $(\mathbf{k}, s)$ present in the lattice at $T = 1/k_B T$.
Note: $n_s(\mathbf{k})$ is the Bose-Einstein distribution function (with $\mu = 0$) $\implies$ phonons obey boson statistics!

Lattice's Specific Heat Capacity

$$u = \frac{1}{V}\sum_{\mathbf{k}s} \left(\frac{1}{e^{-\beta\hbar\omega_s(\mathbf{k})}-1} + \frac{1}{2} \right)\hbar\omega_s(\mathbf{k}) \qquad \text{(review: internal energy)}$$

$$c_V = \frac{\partial u}{\partial T} = \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(k)}-1}$$

Complication: the above general expression for specific heat cannot be evaluated analytically.
Solution: analyze c_V in limit cases or using approximations.

Phonon Specific Heat: High-Temperature Limit

Heuristically: as $T \to \infty$ every normal mode will be excited and quantization of modes grows negligible, so we expect a classical result independent of $\hbar$.
Consider a 3D lattice with N lattice sites and $3p$ branches

$$c_V = \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} \qquad \text{(for review)}$$

Let $x \equiv \beta\hbar\omega_s(\mathbf{k}) \implies x \ll 1$ for $T \to \infty$

$$\frac{1}{e^x-1} \approx \frac{1}{1+x+\frac{x^2}{2}+\frac{x^3}{6}+\cdots-1} = \frac{1}{x}\frac{1}{1+\frac{x}{2}+\frac{x^2}{6}} \qquad \text{(for later use)}$$

$$\approx \frac{1}{x}\left[1 - \left(\frac{x}{2} + \frac{x^2}{6} \right) + \left(\frac{x}{2} + \frac{x^2}{6} \right)^2 \right] \qquad (\tfrac{1}{1+y} \approx 1 - y + y^2)$$

$$= \frac{1}{x}\left[1 - \frac{x}{2} + \frac{x^2}{12} + \mathcal{O}(x^3) \right]$$

Use the expansion with c_V and $x = \beta\hbar\omega_s(\mathbf{k})$ to get...

$$c_V \approx \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{\hbar\omega_s(\mathbf{k})\beta}\left[1 - \frac{\hbar\omega_s(\mathbf{k})\beta}{2} + \frac{1}{12}\left(\beta\hbar\omega_s(\mathbf{k}) \right)^2 \right]$$

$$= \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} k_B T\left[1 - \frac{\hbar\omega_s(\mathbf{k})}{2k_B T} + \frac{(\hbar\omega_s(\mathbf{k}))^2}{12(k_B T)^2} \right] \qquad \text{(in terms of } T\text{)}$$

$$= \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} \left[k_B T - \frac{\hbar\omega_s(\mathbf{k})}{2} + \frac{(\hbar\omega_s(\mathbf{k}))^2}{12 k_B T} \right] \qquad \text{(simplifying)}$$

$$= \frac{k_B}{V}\sum_{\mathbf{k}s} \left[1 - \frac{(\hbar\omega_s(\mathbf{k}))^2}{12(k_B T)^2} \right] \qquad \text{(differentiating)}$$

$$\to \frac{k_B}{V}\sum_{\mathbf{k}s} 1 \qquad \text{(as } T \to \infty\text{)}$$

$$= \frac{k_B}{V} 3pN \qquad (N \text{ values of } \mathbf{k} \text{ and } 3p \text{ branches})$$

Let $n = \frac{3Np}{V}$ denote number density of ions in crystal to get...

$$c_V = 3nk_B \qquad \textbf{(high-temperature limit)}$$

Interpretation: $c_V = 3nk_B$ is the law of Dulong and Petit

Phonon Specific Heat: Low-Temperature Limit

$$c_V = \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} \qquad \text{(for review)}$$

$$\approx \frac{\partial}{\partial T}\sum_s \iiint_{\text{BZ}} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1}\frac{d^3\mathbf{k}}{(2\pi)^3} \qquad \text{(approximating } \sum \text{ with } \int\text{)}$$

Idea: at low temperature ($k_B T \ll \hbar\omega_s(\mathbf{k})$) only low-frequency modes are excited. As a result...

- the contribution of acoustic modes far from $\mathbf{k} = \mathbf{0}$ and optical modes (both high-frequency) to specific heat is negligible.

- we may take the integral over all $\mathbf{k}$ space instead of over only the first Brillouin zone.

- we may approximate $\omega_s(\mathbf{k})$ with a linear dispersion of the form...

$$\omega_s(\mathbf{k}) \approx c_s(\hat{\mathbf{k}})k \qquad \text{(low-temperature approximation)}$$

Validity: the approx. holds as long as $k_B T \ll \hbar\omega_s(\mathbf{k})$ for all $\omega_s(\mathbf{k})$ that are poorly approximated by $\omega_s(\mathbf{k}) \approx c_s(\hat{\mathbf{k}})k$.

$$c_V \approx \frac{1}{8\pi^3}\frac{\partial}{\partial T}\sum_s \iiint \frac{\hbar c_s(\hat{\mathbf{k}})k}{e^{\beta\hbar c_s(\hat{\mathbf{k}})k}-1} d^3\mathbf{k} \qquad \text{(for low temperatures)}$$

$$= \frac{1}{8\pi^3}\frac{\partial}{\partial T}\sum_s \iiint \frac{\hbar c_s(\hat{\mathbf{k}})k}{e^{\beta\hbar c_s(\hat{\mathbf{k}})k}-1}k^2\,dk\,d\Omega \qquad \text{(to spherical coords.)}$$

Let $x \equiv \beta\hbar c_s(\hat{\mathbf{k}})k$ (new variable)

$$c_V = \frac{1}{8\pi^3}\frac{\partial}{\partial T}\sum_s \iint \frac{d\Omega}{\beta^4\hbar^3 c_s(\hat{\mathbf{k}})}\int_0^\infty \frac{x^3}{e^x-1}\,dx \qquad \text{(in terms of } x\text{)}$$

$$\int_0^\infty \frac{x^3}{e^x-1}\,dx = \frac{\pi^4}{15} \qquad \text{(tabulated integral)}$$

Let $\frac{1}{c^3} \equiv \frac{1}{3}\sum_s \iint \frac{d\Omega}{4\pi c_s^3(\hat{\mathbf{k}})}$ (average speed over solid angle)

$$c_V = \frac{1}{8\pi^3}\frac{1}{\hbar^3}\frac{\partial}{\partial T}\frac{1}{\beta^4}\left(\frac{3\cdot 4\pi}{c^3} \right)\cdot\frac{\pi^4}{15} \qquad \text{(in terms of } c \text{ and integral)}$$

$$= \frac{\pi^2}{10}\frac{1}{(\hbar c)^3}\frac{\partial}{\partial T}(k_B T)^4 \qquad \text{(simplifying)}$$

$$= \frac{2\pi^2}{5}k_B \left(\frac{k_B T}{\hbar c} \right)^3 \qquad \textbf{(low-temperature limit)}$$

Primary result: $c_V \propto T^3$ for at low temperatures

Debye Approximation

Goal: develop an approximate interpolation scheme connecting the low- and high-temperature limits of phonon c_V.

General Considerations

Consider the dispersion of a 3D lattice with N lattice sites and a basis with p atoms per primitive cell.

$$N_{\text{ion}} = pN \qquad \text{(number of ions in the crystal)}$$

The Debye approximation is to...

- Approximate the three acoustic branches with three *identical* linear branches of the form $w = ck$, ranging from $\mathbf{k} = \mathbf{0}$ to a *finite* value $k = k_D$. k_D is the *Debye wave vector* and generally lies outside the first BZ.

- Neglect optical branches.
  Heuristic justification: the portions of linear branches beyond first BZ approximate the otherwise-neglected optical branches

Review: the Fermi wave vector k_F is defined as the smallest radius in $\mathbf{k}$ space enclosing all N_e occupied electron levels.

$$N_e = 2\cdot\frac{V_F}{\Delta\mathbf{k}} = 2\cdot\frac{4\pi k_F^3}{3}\frac{V}{8\pi^3} \qquad \text{(factor 2 from } e^- \text{ spin)}$$

$$= \frac{k_F^3}{6\pi^2}V \qquad \text{(Fermi wave vector for } e^-\text{)}$$

$$\implies k_F^3 = 6\pi^2\frac{N_e}{V} = 6\pi^2 n_e \qquad (k_F \text{ in terms of } e^- \text{ density)}$$

Analogy: the Debye wave vector is defined as the smallest radius in $\mathbf{k}$ space enclosing exactly N_{ion} wave vectors.

$$N_{\text{ion}} = \frac{V_D}{\Delta\mathbf{k}} = \frac{4\pi k_D^3}{3}\frac{V}{8\pi^3} \qquad \text{(phonons are spin-less; no 2 factor)}$$

$$= \frac{k_D^3}{6\pi^2}V \qquad \text{(Debye wave vector for phonons)}$$

$$\implies k_D^3 = 3\pi^2\frac{N_{\text{ion}}}{V} = 3\pi^2 n_{\text{ion}} \qquad (k_D \text{ in terms of ion density)}$$

Debye Approximation: General Expression

Let $\frac{1}{c^3} \equiv \frac{1}{3}\sum_s \iint \frac{d\Omega}{4\pi c_s(\hat{\mathbf{k}})^3}$ (average c over acoustic branches)

$$c_V = \frac{1}{V}\frac{\partial}{\partial T}\sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} \qquad \text{(in general)}$$

$$\approx \frac{\partial}{\partial T}\sum_s \iiint_{\text{BZ}} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1}\frac{d^3\mathbf{k}}{(2\pi)^3} \qquad \text{(approximating } \sum \text{ with } \int\text{)}$$

$$\approx 3\cdot\frac{1}{8\pi^3}\frac{\partial}{\partial T}\iiint_{\text{BZ}} \frac{\hbar ck}{e^{\beta\hbar\omega k}-1} d^3\mathbf{k} \qquad \text{(Debye: } \omega_s(\mathbf{k}) \to ck \;\forall\; 3\; s\text{)}$$

$$\approx \frac{3}{8\pi^3}\frac{\partial}{\partial T}\iiint \frac{\hbar ck}{e^{\beta\hbar\omega k}-1} d^3\mathbf{k} \qquad \text{(integrate over all } \mathbf{k}\text{)}$$

31

$$= \frac{3}{8\pi^3} \frac{\partial}{\partial T} \iint \mathrm{d}\Omega \int_0^{k_\mathrm{D}} \frac{\hbar c k}{e^{\beta\hbar\omega_k} - 1} k^2 \,\mathrm{d}k \qquad \text{(to spherical coords.)}$$

$$= \frac{3 \cdot 4\pi}{8\pi^3} \frac{\partial}{\partial T} \int_0^{k_\mathrm{D}} \frac{\hbar c k^3}{e^{\beta\hbar\omega_k} - 1} \,\mathrm{d}k \qquad \text{(integrating over } \mathrm{d}\Omega\text{)}$$

$$= \frac{3}{2\pi^2} \frac{(\hbar c)^2}{k_\mathrm{B} T^2} \int_0^{k_\mathrm{D}} \frac{k^4 e^{\beta\hbar c k}}{(e^{\beta\hbar c k} - 1)^2} \,\mathrm{d}k \qquad \text{(differentiating)}$$

Let $x = \beta\hbar c k$ \hfill (new variable)

$x_\mathrm{D} \equiv x(k_\mathrm{D}) = \frac{\hbar c}{k_\mathrm{B} T} k_\mathrm{D}$ \hfill (integration limit)

$k_\mathrm{B}\Theta_\mathrm{D} = \hbar c k_\mathrm{D}$ \hfill (definition of Debye temperature Θ_D)

$$c_\mathrm{V} = \frac{3}{2\pi^2} \frac{k_\mathrm{B}(\hbar c)^2 (k_\mathrm{B} T)^5}{(k_\mathrm{B} T)^2 (\hbar c)^5} \int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \qquad \text{(in terms of } x\text{)}$$

$$= \frac{3k_B}{2\pi^2} \left(\frac{k_\mathrm{B} T}{\hbar c}\right)^3 \int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \qquad \text{(simplifying)}$$

Multiply above/below by $(k_\mathrm{B}\Theta_\mathrm{D})^3$ and use $k_\mathrm{D}^3 = 6\pi^2 n_\mathrm{ion}$ to get...

$$c_\mathrm{V} = 9 k_\mathrm{B} n_\mathrm{ion} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3 \int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \qquad \textbf{(Debye: general result)}$$

$$= \frac{3k_B}{2\pi^2} \left(\frac{k_\mathrm{B} T}{\hbar c}\right)^3 \int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \qquad \text{(alternate expression)}$$

Problem: the expression is not analytically solvable.

Resolution: observe limit cases of high and low temperature.

Debye Approximation: Low-Temperature Limit

$x_\mathrm{D} = \frac{\hbar c}{k_\mathrm{B} T} k_\mathrm{D}$ \hfill (for review)

$\implies x_\mathrm{D} \to \infty$ as $T \to 0$

$\int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \to \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x = \frac{4\pi^4}{15}$ \hfill (tabulated integral)

$$c_\mathrm{V} = \frac{3k_B}{2\pi^2} \left(\frac{k_\mathrm{B} T}{\hbar c}\right)^3 \int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \qquad \text{(generally)}$$

$$\to \frac{3k_B}{2\pi^2} \left(\frac{k_\mathrm{B} T}{\hbar c}\right)^3 \frac{4\pi^4}{15} \qquad \text{(as } T \to 0\text{)}$$

$$= \frac{2\pi^2}{5} \left(\frac{k_\mathrm{B} T}{\hbar c}\right)^3 k_\mathrm{B} \qquad \text{(Debye result: low-temp. limit)}$$

$$= \frac{12\pi^4}{5} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3 n_\mathrm{ion} k_\mathrm{B} \qquad \text{(in terms of } \Theta_\mathrm{D}\text{)}$$

Note: agrees with the result in derived earlier in Phonon Specific Heat: Low-Temperature Limit.

Debye Approximation: High-Temperature Limit

$x_\mathrm{D} = \frac{\hbar c}{k_\mathrm{B} T} k_\mathrm{D}$ \hfill (for review)

$x_\mathrm{D} \to 0$ as $T \to \infty$

$x_\mathrm{D} = \Theta_\mathrm{D}/T$ \hfill (in general, for later use)

$\int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \to 0$ \hfill (as $T \to \infty$)

Plan: expand integral for small x to get...

$$\int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \approx \int_0^{x_\mathrm{D}} \frac{x^4 \cdot 1}{(1 + x - 1^2)} = \int_0^{x_\mathrm{D}} x^2 \,\mathrm{d}x$$

$$= \frac{x_\mathrm{D}^3}{3} = \frac{1}{3}\left(\frac{\Theta_\mathrm{D}}{T}\right)^3 \qquad \text{(using } x_\mathrm{D} = \Theta_\mathrm{D}/T\text{)}$$

$$c_\mathrm{V} = 9 k_\mathrm{B} n_\mathrm{ion} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3 \int_0^{x_\mathrm{D}} \frac{x^4 e^x}{(e^x - 1)^2} \,\mathrm{d}x \qquad \text{(in general)}$$

$$\to 9 k_\mathrm{B} n_\mathrm{ion} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3 \frac{1}{3}\left(\frac{\Theta_\mathrm{D}}{T}\right)^3 \qquad \text{(as } T \to \infty\text{)}$$

$$= 3 n_\mathrm{ion} k_\mathrm{B} \qquad \text{(Debye result: high-temp. limit)}$$

Note: agrees with the result in derived earlier in Phonon Specific Heat: High-Temperature Limit.

Comparing Electron and Photon Specific Heats

Goal: determine the temperature at which the contribution of phonons to c_V surpasses the contribution of electrons.

$c_\mathrm{V}^\mathrm{ph} = \frac{12\pi^4}{5} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3 n_\mathrm{ion} k_\mathrm{B}$ \hfill (phonon specific heat; low T)

Review: from "**Sommerfeld Expansion of Heat Capacity**"...

$c_\mathrm{V}^\mathrm{el} = \frac{\pi^2}{2} \frac{n_\mathrm{e}}{E_\mathrm{F}} k_\mathrm{B}^2 T$ \hfill (electron specific heat)

$= \frac{\pi^2}{2} \frac{T}{T_\mathrm{F}} n_\mathrm{e} k_\mathrm{B}$ \hfill (in terms of Fermi temp. $T_\mathrm{F} = E_\mathrm{F}/k_\mathrm{B}$)

Divide c_V^el by c_V^ph to get...

$\frac{c_\mathrm{V}^\mathrm{el}}{c_\mathrm{V}^\mathrm{ph}} = \frac{5}{24\pi^4} \frac{n_\mathrm{el}}{n_\mathrm{ion}} \frac{\Theta_\mathrm{D}^3}{T^2 T_\mathrm{F}}$

$= \frac{5z}{24\pi^4} \frac{\Theta_\mathrm{D}^3}{T^2 T_\mathrm{F}}$ \hfill ($z = n_\mathrm{el}/n_\mathrm{ion}$ is number conduction e^- per ion)

Let T_C denote crossover temperature where $c_\mathrm{V}^\mathrm{el}/c_\mathrm{V}^\mathrm{ph} = 1$

$T_\mathrm{c} = \sqrt{\frac{5z}{24\pi^4} \frac{\Theta_\mathrm{D}}{T_\mathrm{F}}} \,\Theta_\mathrm{D}$ \hfill (crossover btwn. dominance of c_V^el / c_V^ph)

c_V^ph dominates above T_c and c_V^el below T_c

For orientation: $T_\mathrm{c} \sim 5\,\mathrm{K}$ to $10\,\mathrm{K}$ \hfill (in typical solids)

Introduction to Anharmonic Effects

For review: the analysis of lattice oscillations so far was *harmonic*, involving an expansion of lattice potential energy U about its equilibrium position only to *leading order* in displacement from equilibrium.

Motivation: many observed properties of solids emerge theoretically only from higher-order *anharmonic corrections* in the expansion of U.

Some phenomena requiring anharmonic corrections:

- thermal expansion of solids

- temperature dependence of elastic constants

- deviation of c_V^ph from $3 n_\mathrm{ion} k_\mathrm{B}$ for $T \gg \Theta_\mathrm{D}$

- finite (non-zero) peak width in neutron scattering spectra

Thermal Expansion in a 1D Lattice

Goal: provide a simple model of thermal expansion in a 1D monoatomic lattice in which deviation of ions from equilibrium sites is proportional to T.

General Considerations

Let x_0 denote equilibrium spacing between lattice sites.

Let x_1 denote post-expansion spacing btwn. lattice sites.

$x \equiv x_1 - x_0$ (new variable, moves origin to x_0 for shorthand)

$U(x) = U_\mathrm{eq} + cx^2 - gx^3 - fx^4$ (quoted: ansatz for potential)

$\equiv cx^2 - gx^3 - fx^4$ \hfill (set eq. potential to zero)

$|gx^3|, |fx^4| \ll |cx^2|$ \hfill (regime of validity)

Thermal Expansion

Plan: find expected value $\langle x \rangle$ from eq. position for small x

Note: calculation is highly approximate, results are qualitative.

$Z = \int_0^\infty e^{-\beta E} \,\mathrm{d}E$ \hfill (partition function)

$= \int_{-\infty}^\infty e^{-\beta U(x)} \,\mathrm{d}x$ \hfill (in terms of x)

$\langle x \rangle = \frac{1}{Z} \int_{-\infty}^\infty x e^{-\beta U(x)} \,\mathrm{d}x$ \hfill (expected value of x)

$e^{-\beta U(x)} = e^{-\beta c x^2} e^{+\beta(g x^3 + f x^4)}$ \hfill (auxiliary approximation)

$\approx e^{-\beta c x^2}(1 + \beta g x^3 + \beta f x^4)$ \hfill (for small x)

$\approx e^{-\beta c x^2}$ \hfill (neglecting x^3 and x^4)

$\langle x \rangle = \frac{\int_{-\infty}^\infty x e^{-\beta U(x)} \,\mathrm{d}x}{\int_{-\infty}^\infty e^{-\beta U(x)} \,\mathrm{d}x}$ \hfill (review: exp. value of x)

$\approx \frac{\int_{-\infty}^\infty x \left(1 + \beta g x^3 + \beta f x^4\right) e^{-\beta c x^2} \,\mathrm{d}x}{\int_{-\infty}^\infty e^{-\beta c x^2} \,\mathrm{d}x}$ \hfill (with above approx.)

Shortcut: only even terms in numerator integrate to non-zero

$\langle x \rangle = \frac{\int_{-\infty}^\infty \beta g x^4 e^{-\beta c x^2} \,\mathrm{d}x}{\int_{-\infty}^\infty e^{-\beta c x^2}}$ \hfill (odd terms integrate to zero)

Let $y^2 = \beta c x^2$ \hfill (new integration variable)

$\langle x \rangle = \frac{g\sqrt{\beta c}}{\sqrt{\beta^3 c^5}} \frac{\int_{-\infty}^\infty y^4 e^{-y^2} \,\mathrm{d}y}{\int_{-\infty}^\infty e^{-y^2} \,\mathrm{d}y}$ \hfill (in terms of y)

$\int_{-\infty}^\infty e^{-y^2} \,\mathrm{d}y = \sqrt{\pi}$ \hfill (tabulated integral)

$\int_{-\infty}^\infty x^4 e^{-y^2} \,\mathrm{d}y = \frac{3}{4}\sqrt{\pi}$ \hfill (tabulated integral)

$\implies \langle x \rangle = \frac{3}{4} \frac{g}{\beta c^2}$ \hfill (result: expected deviation from eq.)

$= \frac{3g}{4c^2} k_\mathrm{B} T \propto T$ \hfill (in terms of T)

Main lesson: deviation of lattice sites from equilibrium position increases linearly with increasing T (as in experiment).

Note: $U(x)$ must be asymmetric about eq. position for $\langle x \rangle \neq 0$.

Kinetic Theory of Phonon Heat Conduction

General Considerations

- consider only a monoatomic Bravais lattice

- model dispersions with the Debye approx. $w = ck$

- phonons interact via scattering processes parameterized by a mean free time τ between scatterings

- $\ell = c\tau$ is phonon mean free path between scattering,

where c is average phonon speed

Assumption: post-scattering phonon energy depends only on temperature at position of scattering.

Model and Geometry
Consider a lattice with a temperature gradient in the x direction.
$\mathbf{j} = j\,\hat{\mathbf{e}}_x$ (heat current density, assuming 1D ∇T)
Consider an arbitrary point at $x = x_0$ in the lattice.
Assumption: heat current at x_0 depends only on phonons scattering a radial distance ℓ from x_0.

High T Low T

$-\dfrac{\mathrm{d}T}{\mathrm{d}x}$ [Ashcroft]
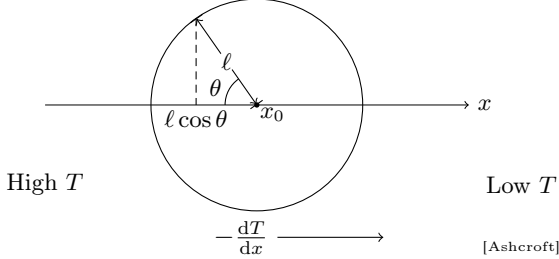
Finding Heat Current Density
Let $u(x)$ denote energy density at position x
Let c denote post-scattering phonon velocity
$c_x = c\cos\theta$ (projection of c onto x axis)
$j = \langle c_x \cdot u(x_0 - \ell\cos\theta)\rangle_\Omega$ (heat current density at x_0)
$ = \frac{1}{4\pi}\iint c_x \cdot u(x_0 - \ell\cos\theta)\,\mathrm{d}\Omega$ (avg. over solid angle)
$ = \frac{2\pi}{4\pi}\int_0^\pi (c\cos\theta)\cdot u(x_0 - \ell\cos\theta)\sin\theta\,\mathrm{d}\theta$ (2π from φ)
Let $y \equiv \cos\theta$ (new integration variable)
$j = \frac{c}{2}\int_{-1}^{1} y\, u(x_0 - \ell y)\,\mathrm{d}y$ (in terms of y)
$ = \frac{c}{2}\int_{-1}^{1} y\left[u(x_0) - \ell y \frac{\partial u}{\partial x}\big|_{x_0} + \mathcal{O}(\ell y)^2\right]\mathrm{d}y$ (expanding $u(x)$)
$ \approx -\frac{c\ell}{3}\cdot\frac{\partial u}{\partial x}\big|_{x_0}$ (evaluating integral to $\mathcal{O}(\ell y)$)
$ = -\frac{c\ell}{3}\frac{\partial u}{\partial T}\big|_{x_0}\frac{\partial T}{\partial x}\big|_{x_0}$ (chain rule)
$ = -\frac{c\ell}{3}c_{\mathrm{V}}(x_0)\frac{\partial T}{\partial x}$ (recognizing $c_{\mathrm{V}} = \frac{\partial u}{\partial T}$)
$j(x) = -\frac{c\ell}{3}c_{\mathrm{V}}(x)\frac{\partial T}{\partial x}$ (result: phonon heat current)
Let $\kappa \equiv \frac{c\ell}{3}c_{\mathrm{V}} = \frac{c^2\tau}{3}c_{\mathrm{V}}$ (thermal conductivity)
$j(x) = -\kappa\frac{\partial T}{\partial x}$ (in terms of thermal conductivity)

Temperature Dependence of Thermal Conductivity
$\kappa = \frac{c\ell}{3}c_{\mathrm{V}} = \frac{c^2\tau}{3}c_{\mathrm{V}}$ (review: thermal conductivity)
Contributions to $\kappa(T)$ arise from...

- $c_{\mathrm{V}}(T)$ (phonon heat capacity)

- $\tau(T)$ (T-dependence of scattering mean free time)

- $c(T) \approx$ constant (neglect T-dependence of phonon speed)
  Justification: c depends on crystal's elastic constants, which are only weakly temperature dependent.

Contributions to $\tau(T)$ arise from...

- phonon-phonon scattering

- impurities in the crystal (which we'll neglect)

- phonon scattering from crystal surface (which we'll neglect)

Plan: only analyze phonon-phonon scattering in any detail.

Conservations Laws for Phonon Scattering
$n_{\mathbf{k}s}$ is pre-scattering phonon occupation number
$n'_{\mathbf{k}s}$ is post-scattering phonon occupation number
$\omega_s(\mathbf{k})$ is frequency of phonon in s-th branch with WV $\mathbf{k}$
Phonon scattering obeys the following conservation laws...

1. $\sum\limits_{\mathbf{k}s} n_{\mathbf{k}s}\hbar\omega_s(\mathbf{k}) = \sum\limits_{\mathbf{k}s} n'_{\mathbf{k}s}\hbar\omega_s(\mathbf{k})$ (conservation of energy)

2. $\sum\limits_{\mathbf{k}s}\mathbf{k}n_{\mathbf{k}s} = \sum\limits_{\mathbf{k}s}\mathbf{k}n'_{\mathbf{k}s} + \mathbf{K}$ (cons. of crystal momentum)
   Note: crystal momentum is conserved only up to a reciprocal lattice vector $\mathbf{K}$. Intuition: if two phonons combine to have $\mathbf{k}$ outside first BZ, $\mathbf{K}$ is needed to map the combined $\mathbf{k}$ back into the first BZ.

Sums are taken over $\mathbf{k}$ in the first Brillioun zone!

Phonon MFT: High-Temperature Limit
Consider behavior of $n_s(\mathbf{k})$ for $T \gg \Theta_{\mathrm{D}}$...
$n_s(\mathbf{k}) = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})}-1}$ (in general (Bose-Einstein distribution))
$\phantom{n_s(\mathbf{k})} \approx \frac{1}{(1+\beta\hbar\omega_s(\mathbf{k}))-1}$ (expanding exp for $k_{\mathrm{B}}T \gg \hbar\omega_s(\mathbf{k})$)
$\phantom{n_s(\mathbf{k})} = \frac{k_{\mathrm{B}}T}{\hbar\omega_s(\mathbf{k})}$ (high-temperature limit)
Assumption: $\tau \sim 1/\sum n_s(\mathbf{k})$. Interpretation: scattering increases (and τ decreases) with increasing phonon number $n_{\mathbf{k}s}$. Since $\tau \sim \frac{1}{n_s(\mathbf{k})}$ and $n_s(\mathbf{k}) \sim T$, for $T \gg \Theta_{\mathrm{D}}$ MFT τ scales as...
$\tau \sim \frac{1}{T}$ (theoretical phonon MFT for $T \gg \Theta_{\mathrm{D}}$)
$\tau \sim \frac{1}{T^x}$ with $x \in (1,2)$ (typical measured behavior)

Phonon MFT: Low-Temperature Limit I
$\sum\limits_{\mathbf{k}s}\mathbf{k}n_{\mathbf{k}s} = \sum\limits_{\mathbf{k}s}\mathbf{k}n'_{\mathbf{k}s} + \mathbf{K}$ (review: conservation of $\mathbf{k}$)
Review: $\mathbf{K}$ maps post-scattering wave vector $\sum\limits_{\mathbf{k}s}\mathbf{k}n'_{\mathbf{k}s}$ back into the first Brillioun zone (if necessary)
Idea: for $T \ll \Theta_{\mathrm{D}}$, only phonons with frequency $\omega_s(\mathbf{k}) \ll \omega_{\mathrm{D}}$ and wave vector $k \ll k_{\mathrm{D}}$ occur appreciably.
Consequence: the k of all phonons participating in scattering processes are $\ll k_{\mathrm{D}} \implies$ the total post-scattering wave vector $\sum\limits_{\mathbf{k}s}\mathbf{k}n'_{\mathbf{k}s}$ will lie *inside* the first Brillioun zone $\implies \mathbf{K} = \mathbf{0}$.

Terminology

- *normal processes* are scattering processes with $\mathbf{K} = \mathbf{0}$

- *umklapp processes* are scattering processes with $\mathbf{K} \neq \mathbf{0}$

Normal processes dominate at $T \ll \Theta_{\mathrm{D}}$ because $\mathbf{K} = \mathbf{0}$
$\sum\limits_{\mathbf{k}s}\mathbf{k}n_{\mathbf{k}s} = \sum\limits_{\mathbf{k}s}\mathbf{k}n'_{\mathbf{k}s}$ (normal processes)
$\implies$ normal processes conserve crystal momentum exactly
Plan: digress somewhat to discuss phonon heat current density, equilibrium, and normal processes. Return to MFT τ in section .

Phonon Heat Current Density
$u = \frac{1}{V}\sum\limits_{\mathbf{k}s}\hbar\omega_s(\mathbf{k})$ (lattice's phonon internal energy)
$\mathbf{j}_{\mathrm{ph}} = \frac{1}{V}\sum\limits_{\mathbf{k}s}\hbar\omega_s(\mathbf{k})n_s(\mathbf{k})\nabla_{\mathbf{k}}\omega_s(\mathbf{k})$ (heat current density)
$\phantom{\mathbf{j}_{\mathrm{ph}}} \approx \sum\limits_s \iiint_{\mathrm{BZ}} \hbar\omega_s(\mathbf{k})n_s(\mathbf{k})\nabla_{\mathbf{k}}\omega_s(\mathbf{k})\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}$ (as an integral)
Interpretation: $\mathbf{j}_{\mathrm{ph}}$ is internal energy u times group velocity $\mathbf{v}_{\mathrm{g}} = \nabla_{\mathbf{k}}\omega_s(\mathbf{k})$ times phonon density $n_s(\mathbf{k})$
Idea: $\omega_s(\mathbf{k}) = \omega_s(-\mathbf{k}) \implies \nabla_{\mathbf{k}}\omega_s(\mathbf{k}) = -\nabla_{\mathbf{k}}\omega_s(-\mathbf{k})$
$\implies \omega_s(\mathbf{k})$ is even and $\nabla_{\mathbf{k}}\omega_s(\mathbf{k})$ is odd $\implies$ integrand in $\mathbf{j}_{\mathrm{ph}}$ is odd if $n_s(\mathbf{k})$ is even, i.e. if $n_s(\mathbf{k}) = n_s(-\mathbf{k})$
Conclusion: $\mathbf{j}_{\mathrm{ph}} \neq \mathbf{0}$ only if $n_s(\mathbf{k}) \neq n_s(-\mathbf{k})$ (since the integral of an odd function over its domain (1st BZ for $\mathbf{k}$) is zero).

Normal Processes Preserve Equilibrium
In thermal equilibrium:
$n_s(\mathbf{k}) = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})}-1}$ (in thermal equilibrium)
$\omega_s(\mathbf{k}) = \omega_s(-\mathbf{k}) \implies n_s(\mathbf{k}) = n_s(-\mathbf{k})$ (in equilibrium)
Conclusion: $n_s(\mathbf{k})$ is even in equilibrium, so $\mathbf{j}_{\mathrm{eq}} = \mathbf{0}$.

Meanwhile: $\mathbf{k}_{\mathrm{tot}} = \mathbf{0}$ if $n_s(\mathbf{k})$ is even, since $n_s(\mathbf{k})$ even $\implies \mathbf{k} \cdot n_s(\mathbf{k})$ is odd, which vanishes during $\sum_{\mathbf{k}\in\mathrm{BZ}}$
Conclusion: $\mathbf{k}_{\mathrm{tot}} = \mathbf{0}$ in equilibrium (when $n_s(\mathbf{k})$ is even).

Meanwhile: consider normal processes only.

$$\sum_{\mathbf{k}s} \mathbf{k} n_s(\mathbf{k}) = \sum_{\mathbf{k}s} \mathbf{k} n'_s(\mathbf{k}) \qquad \text{(for normal processes)}$$

$$\implies \frac{\mathrm{d}}{\mathrm{d}t} \mathbf{k}_{\text{tot}} = \frac{\mathrm{d}}{\mathrm{d}t} \sum_{\mathbf{k}s} \mathbf{k} n_s(\mathbf{k}) = \mathbf{0} \qquad (\mathbf{k}_{\text{tot}} \text{ conserved})$$

Conclusion: normal processes conserve total wave vector.

Summary of results

- $n_s(\mathbf{k})$ is even in equilibrium

- $\mathbf{j}_{\text{ph}} = \mathbf{0}$ in equilibrium (by definition and by analysis)
  $\mathbf{j}_{\text{ph}} \neq \mathbf{0}$ out of equilibrium (by definition and by analysis)

- $\mathbf{k}_{\text{tot}}$ must equal $\mathbf{0}$ in equilibrium

- Normal processes preserve total crystal momentum

Since normal processes conserve $\mathbf{k}_{\text{tot}}$, normal processes alone cannot return a state with non-zero $\mathbf{k}_{\text{tot}}$ to equilibrium $\mathbf{k}_{\text{tot}} = \mathbf{0}$. Result: considering *normal processes only*, the phonon thermal conductivity of crystal is infinite, since a nonzero $\mathbf{k}_{\text{tot}}$ and thus nonzero $\mathbf{j}_{\text{ph}}$ remain nonzero for all t!

Return to Equilibrium via Umklapp Processes

Review: normal processes alone cannot return a state with non-zero $\mathbf{j}$ to equilibrium $\implies$ umklapp processes must be responsible for return to equilibrium.

Review: normal processes involve phonons with $k \ll k_{\text{D}}$ and thus $\omega_s(\mathbf{k}) \ll \omega_{\text{D}}$. Consequence: umklapp processes involve phonons with $\omega_s(\mathbf{k}) \gtrsim \omega_{\text{D}}$

$$n_s(\mathbf{k}) = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1} \qquad \text{(in general)}$$

$$\sim \frac{1}{e^{\beta\hbar\omega_{\text{D}}} - 1} \qquad \text{(for first occurring umklapp processes)}$$

$$= \frac{1}{e^{\Theta_{\text{D}}/T} - 1} \qquad \text{(in terms of } \Theta_{\text{D}})$$

$$\approx e^{-\Theta_{\text{D}}/T} \qquad \text{(in low-temp limit } T \ll \Theta_{\text{D}})$$

Review: $\tau \sim 1/\sum n_s(\mathbf{k})$. Interpretation: scattering increases (and τ decreases) with increasing phonon number $n_{\mathbf{k}s}$.

Since $\tau \sim \frac{1}{n_s(\mathbf{k})}$ and $n_s(\mathbf{k}) \sim e^{-\Theta_{\text{D}}/T}$, for $T \ll \Theta_{\text{D}}$ the phonon mean free time τ scales as...

$$\tau \sim e^{\Theta_{\text{D}}/T} \qquad \text{(theoretical phonon MFT for } T \ll \Theta_{\text{D}})$$

$$\tau \sim e^{T_0/T} \text{ with } T_0 \sim \Theta_{\text{D}} \qquad \text{(typical measured behavior)}$$

Phonon MFT: Low-Temperature Limit II

$$\tau \sim e^{\Theta_{\text{D}}/T} \qquad \text{(review: phonon MFT for } T \ll \Theta_{\text{D}})$$

In words: phonon-phonon scattering mean free time τ increases exponentially for $T \ll \Theta_{\text{D}}$.

Naive conclusion: phonon thermal conductivity $\kappa \propto T$ increases exponentially as $T \to 0\,\text{K}$.

- In practice: as $T \to 0\,\text{K}$, phonon-phonon scattering τ is dominated by τ for phonon-impurity and phonon-surface scattering, and total τ_{tot} remains finite as $T \to 0\,\text{K}$

- Additionally: phonon scattering MFP $\ell \propto 1/\tau$ is bounded above by finite crystal size, so τ reaches a constant max. value as $T \to 0\,\text{K}$.