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# 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  $\Lambda$  is the set of points  $\{\mathbf{R}\} \subset \mathbb{R}^3$  given by  $\Lambda \equiv \{\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \mid n_i \in \mathbb{Z}\}$ , where...

$n_1, n_2, n_3 \in \mathbb{Z}$  are arbitrary integers  
 $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  are linearly independent vectors spanning the Bravais lattice and are called *primitive vectors*.

- 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.  $\Lambda = \{\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3\}$  (positions of PUCs)  
Mathematical definition: the crystal's PUC is the smallest region of space the tessellates 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.

$\mathbf{r}_n^{(j)} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 + \mathbf{d}_j$  (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  $\Lambda = \{\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3\}$  (positions of PUCs)

- PUCs contain exactly one 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 region of space spanned by a BL's primitive vectors  
Mathematically: the region  $\Omega_{pp} \subset \mathbb{R}^3$  given by

$\Omega_{pp} \equiv \{\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3; x_i \in [0, 1)\}$

## Conventional Unit Cell

Constructed to display lattice's full symmetry properties

Generally larger than primitive unit cell

Volume is an integer multiple of PUC volume  $V_0$

## Wigner-Seitz Unit Cell

The region of space for which a given site in the Bravais lattice

is the closest lattice point

Mathematically: the region  $\Omega_{\text{WS}} \subset \mathbb{R}^3$  given by

$$\Omega_{\text{WS}} \equiv \{\mathbf{r} \in \mathbb{R}^3: |\mathbf{r}| < |\mathbf{r} - \mathbf{R}| \text{ for all } \mathbf{R} \in \Lambda\}$$

(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  $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$

$$\mathbf{T}_{\mathbf{n}} = n_1 \mathbf{v}_1 + n_2 \mathbf{v}_2 + n_3 \mathbf{v}_3 \quad (\text{general translation operator})$$

$\mathbf{v}_i \in \mathbb{R}^3$  are arbitrary vectors

$$\mathbf{n} = (n_1, n_2, n_3) \text{ where } n_1, n_2, n_3 \in \mathbb{Z}$$

$\mathbf{T}_{\mathbf{n}}$  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...

$$\mathbf{T}_{\mathbf{n}} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (\text{BL invariant if } \{\mathbf{v}_i\} = \{\mathbf{a}_i\})$$

### 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

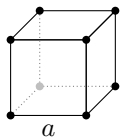
### Simple Cubic (SC)

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

$$N_c = 6 \quad (\text{coordination number})$$



$$\mathbf{a}_1 = a \hat{\mathbf{x}}$$

$$\mathbf{a}_2 = a \hat{\mathbf{y}}$$

$$\mathbf{a}_3 = a \hat{\mathbf{z}}$$

### Body-Centered Cubic (BCC)

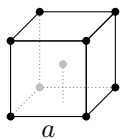
The conventional unit cell is a cube with side lengths  $a$ .

Lattice sites occur at each cube vertex and at cube center

Wigner-Seitz cell is a truncated octahedron

Examples: Ba, Cr, Cs, Fe, K

$$N_c = 8 \quad (\text{coordination number})$$



$$\mathbf{a}_1 = a \hat{\mathbf{x}}$$

$$\mathbf{a}_2 = a \hat{\mathbf{y}}$$

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

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

### 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)



$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

### 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.

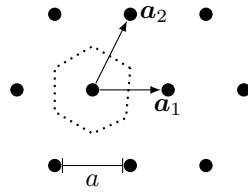
Formulation: FCC primitive vectors plus the basis  $\mathbf{d}_1 = \mathbf{0}$  and  $\mathbf{d}_2 = \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$

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



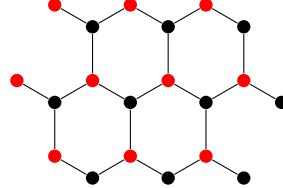
$$\mathbf{a}_1 = a \hat{\mathbf{x}}$$

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

### The Honeycomb Structure

Structure: Two hexagonal lattice sites superimposed on each other, one shifted relative to the other by  $\frac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}/3)$ .

The honeycomb structure is not a Bravais lattice!



$$\mathbf{a}_1 = a \hat{\mathbf{x}}$$

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

$$\mathbf{d}_1 = \hat{\mathbf{0}}$$

$$\mathbf{d}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}/3)$$

### 3D Hexagonal Lattice

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

$$\mathbf{a}_1 = a \hat{\mathbf{x}}$$

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

$$\mathbf{a}_3 = c \hat{\mathbf{z}}$$

## Reciprocal Lattice

A reciprocal lattice is defined only in the context of a Bravais lattice. Consider a BL  $\Lambda$  spanned by primitive vectors  $\{\mathbf{a}_i\}$ .

The BL's *reciprocal lattice*  $\Lambda^*$  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)

$$\Lambda^* \equiv \{\mathbf{K} \mid e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda\} \quad (\text{definition of RL})$$

### Interpretation of the Reciprocal Lattice

Consider a Bravais lattice  $\Lambda$  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....

$$e^{i\mathbf{K} \cdot (\mathbf{R} + \mathbf{r})} = e^{i\mathbf{K} \cdot \mathbf{r}} \text{ for all } \mathbf{r} \in \mathbb{R}^3 \text{ and } \mathbf{R} \in \Lambda$$

$$\implies e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda \quad (\text{recovers RL condition})$$

### Reciprocal Primitive Vectors

Consider a Bravais lattice  $\Lambda$  spanned by primitive vectors  $\{\mathbf{a}_i\}$   $\Lambda^* \equiv \{\mathbf{K} \mid e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda\}$  (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*

$$V_0 = |\mathbf{a}_1 \times (\mathbf{a}_2 \times \mathbf{a}_3)| \quad (\text{review: volume of BL's PUC})$$

The RL's *reciprocal primitive vectors*  $\{\mathbf{b}_i\}$  are given by...

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (\text{implicit definition of reciprocal PV})$$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_0} \quad (\text{RPV in terms of PV})$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_0} \quad (\text{RPV in terms of PV})$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_0} \quad (\text{RPV in terms of PV})$$

The BL's PVs  $\{\mathbf{a}_i\}$  are given in terms of  $\{\mathbf{b}_i\}$  by...

$$\mathbf{a}_1 = 2\pi \frac{\mathbf{b}_2 \times \mathbf{b}_3}{V_0^*} \quad (\text{PV in terms of RPV})$$

$$\mathbf{a}_2 = 2\pi \frac{\mathbf{b}_3 \times \mathbf{b}_1}{V_0^*} \quad (\text{PV in terms of RPV})$$

$$\mathbf{a}_3 = 2\pi \frac{\mathbf{b}_1 \times \mathbf{b}_2}{V_0^*} \quad (\text{PV in terms of RPV})$$

$$V_0^* = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)| \quad (\text{volume of reciprocal PUC})$$

$$= (2\pi)^3 / V_0 \quad (\text{in terms of } V_0)$$

### Verifying Definition of Reciprocal Primitive Vectors

Consider a Bravais lattice  $\Lambda$  spanned by primitive vectors  $\{\mathbf{a}_i\}$

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (\text{definition of reciprocal PVs } \{\mathbf{b}_j\})$$

$$\mathbf{K} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \quad (\text{reciprocal lattice vectors})$$

Goal: show the  $\mathbf{b}_i$  are consistent with  $e^{i\mathbf{K} \cdot \mathbf{R}} = 1$  for all  $\mathbf{R} \in \Lambda$

$$\mathbf{K} \cdot \mathbf{R} = (m_i \mathbf{b}_i) \cdot (n_j \mathbf{a}_j) \quad (\text{summation notation})$$

$$= 2\pi(n_1 m_1 + n_2 m_2 + n_3 m_3) \quad (\text{using } \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij})$$

$$= 2\pi N \quad (\text{for some integer } N \in \mathbb{Z})$$

$$\implies e^{i\mathbf{K} \cdot \mathbf{R}} = e^{2\pi i N} = 1 \quad (\text{defs. of } \mathbf{b} \text{ and } \mathbf{K} \text{ are consistent})$$

### First Brillouin Zone

Consider a Bravais lattice  $\Lambda$  spanned by primitive vectors  $\{\mathbf{a}_i\}$

$$\Lambda^* = \{\mathbf{K} \mid e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda\} \quad (\text{the BL's RL})$$

The RL's Wigner-Seitz cell is called the *first Brillouin 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  $\mathbf{K} = \mathbf{0}$ .

$$\Omega_{\text{BZ1}} = \{\mathbf{k} \in (\mathbb{R}^*)^3 : |\mathbf{k}| < |\mathbf{k} - \mathbf{K}| \text{ for all } \mathbf{K} \in \Lambda^*\}$$

### 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  $a$

$$\mathbf{a}_1 = a \hat{\mathbf{x}} \quad (\text{for review})$$

$$\mathbf{a}_2 = a \hat{\mathbf{y}} \quad (\text{for review})$$

$$\mathbf{a}_3 = a \hat{\mathbf{z}} \quad (\text{for review})$$

$$\mathbf{b}_1 = \frac{2\pi}{a} \hat{\mathbf{x}}$$

$$\mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{y}}$$

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

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  $a$

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad (\text{for review})$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \quad (\text{for review})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \quad (\text{for review})$$

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

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

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

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  $a$

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}) \quad (\text{for review})$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}) \quad (\text{for review})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \quad (\text{for review})$$

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

$$\mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$$

$$\mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

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

### Lattice Plates

Consider a Bravais lattice  $\Lambda$  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...

$$\mathbf{K} = \frac{2\pi}{d} \hat{\mathbf{n}} \quad (\text{RL vector for a lattice plane family})$$

For two lattice sites  $\mathbf{R}_i, \mathbf{R}_j$  in the  $i$ -th and  $j$ -th planes...

$$|\mathbf{K} \cdot (\mathbf{R}_i - \mathbf{R}_j)| = 2\pi|i - j| \quad (\text{from geometrical arguments})$$

$$\implies e^{i\mathbf{K} \cdot (\mathbf{R}_i - \mathbf{R}_j)} = 1 \text{ for all } \mathbf{R}_i, \mathbf{R}_j \in \Lambda$$

$$\implies e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \text{ for all } \mathbf{R} \in \Lambda \quad (\text{BL closed under addition})$$

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  $\Lambda$  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.

$$\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3 \quad (\mathbf{K} \text{ in terms of Miller indices})$$

Miller indices are conventionally written in lowest terms, i.e. with greatest common divisor equal to one.

The planes specified by the  $(hkl)$  intersect integer multiples of the points  $\mathbf{a}_1/h$ ,  $\mathbf{a}_2/k$ , and  $\mathbf{a}_3/\ell$ .

$$(n_1 \mathbf{a}_1) \cdot \mathbf{K} = (n_2 \mathbf{a}_2) \cdot \mathbf{K} = (n_3 \mathbf{a}_3) \cdot \mathbf{K} \equiv C \quad (\text{for lattice plane})$$

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...

$$\implies n_1 h = n_2 k = n_3 \ell = C$$

$$\implies h : k : \ell = \frac{1}{n_1} : \frac{1}{n_2} : \frac{1}{n_3} \quad (\text{inverse ratio relationship})$$

### 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.

$$\lambda = \lambda' \quad (\text{assuming elastic scattering})$$

#### Photon Energy for Constructive Interference

Goal: estimate photon energies at which scattered photons will interfere constructively in the crystal lattice

$$a \sim 0.1 \text{ nm} \quad (\text{typical spacing between lattice points})$$

$$\lambda \lesssim a \quad (\text{condition for interference on lattice})$$

$$h\nu = \frac{hc}{\lambda} \gtrsim \frac{hc}{a} \sim \frac{1240 \text{ eV nm}}{0.1 \text{ nm}} \quad (\text{for photon with } \lambda \lesssim a)$$

$$= 12.4 \text{ keV} \quad (\text{min. photon energy for interference})$$

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

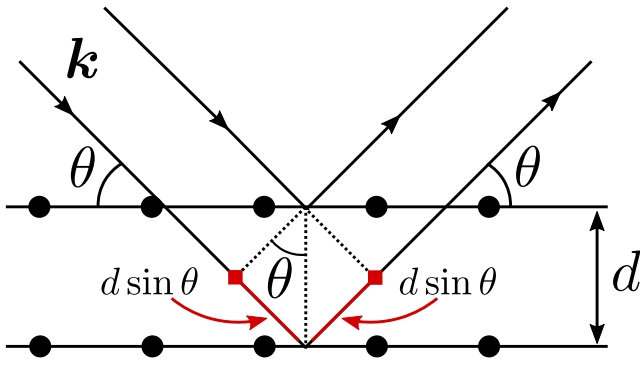


Figure 1: The geometry of Bragg scattering.

### Bragg Interference Condition

Consider x-rays incident at glancing angle  $\theta$  on a family of lattice planes with spacing  $d$ .

$$|k| = |k'| \equiv k \quad (\text{assuming elastic scattering})$$

The difference in path length  $\Delta x$  for x-rays scattering from neighboring lattice planes is...

$$\Delta x = 2d \sin \theta \quad (\text{for neighboring planes})$$

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

$$\Delta \phi = k \Delta x = 2\pi n \quad (\text{constructive interference condition})$$

$$\frac{2\pi}{\lambda} \cdot (2d \sin \theta) = 2\pi n \quad (\text{in terms of wavelength } \lambda)$$

$$2d \sin \theta = n\lambda \quad (\text{Bragg interference condition})$$

### Von Laue Formulation of Scattering

Model: in the von Laue formulation, x-rays scatter from discrete lattice sites rather than from entire lattice planes.

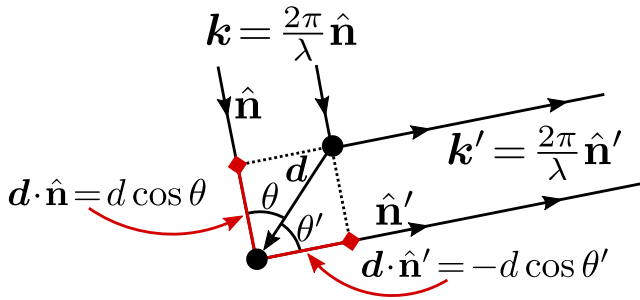


Figure 2: The geometry of von Laue scattering.

### Von Laue Interference Condition

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

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

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

Consider two lattice sites connected by the vector  $d$

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

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

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

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

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

$$\Delta \phi = k \Delta x = 2\pi m \quad (\text{constructive interference condition})$$

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

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

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

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

### Alternate Formulation of the von Laue Condition

Consider a Bravais lattice  $\Lambda$  with reciprocal lattice  $\Lambda^*$

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

$$e^{iR \cdot (k - k')} = e^{2\pi i m} = 1 \quad (\text{exponentiating})$$

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

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

$$k - k' = K \quad (\text{von Laue interference condition})$$

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

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

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

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

### Bragg Plane

From above, an incident WV  $k$  scatters constructively if...

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

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

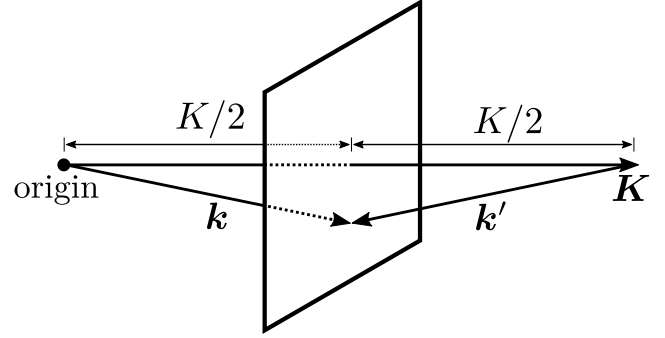


Figure 3: A Bragg plane defined by  $K$ .

### 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  $K = \frac{2\pi n}{d} \hat{n}$  where  $n \in \mathbb{N}$ .

Let  $k$  denote incident wave vector

Let  $k'$  denote scattered wave vector

Let  $\theta$  denote glancing angle between  $k$  and lattice plane

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

The von Laue condition requires a relationship between  $k$ ,  $k'$ , and  $K$  as shown in the figure below...

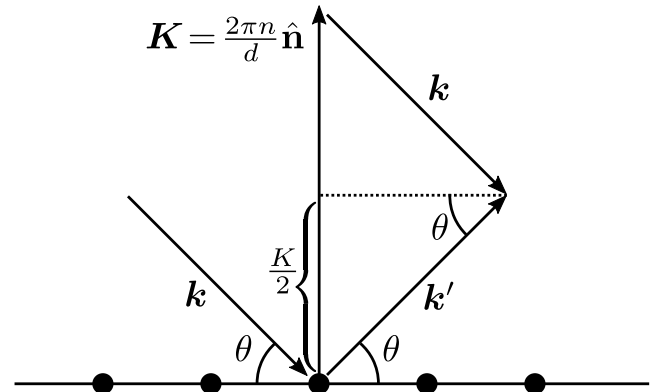


Figure 4: Geometry for showing the equivalence of the Bragg and von Laue interference conditions.

$$\theta = \theta' \quad (\text{law of reflection})$$

$$\implies k' \sin \theta = K/2 \quad (\text{see figure})$$

$$K/2 = k \sin \theta \quad (k = k' \text{ for elastic scattering})$$

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

$$\implies 2d \sin \theta = n\lambda \quad (\text{Bragg condition})$$

### Ewald Sphere Formulation of Scattering

Summary: a geometric method for determining which incident wave vectors  $k$  will scatter constructively from a crystal lattice. The Ewald sphere for a given incident  $k$  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  $k$  points from the origin to sphere's center
- The Ewald sphere has radius  $|k| = 2\pi/\lambda$

If the thus-defined sphere's surface intersects other RL vectors, the incident  $k$  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  $\{\mathbf{d}_j\}$

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

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

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

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

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

$\Delta\phi = \mathbf{K} \cdot (\mathbf{d}_j - \mathbf{d}_k)$  (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)

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

Interpretation: the GSF expresses the extent to which x-rays scattered from the atoms in a given PUC diminish the inten-

sity of the interference peak associated with a given  $\mathbf{K}$  via the von Laue interference condition  $\mathbf{k} - \mathbf{k}' = \mathbf{K}$ .

**TODO: Example: GSF for a BCC Lattice**

### 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  $\rho_j$  denote  $j$ -th atom's electron cloud charge density

Let  $Z_j$  denote  $j$ -th atom's atomic number

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

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

$$f_j(\mathbf{K}) = -\frac{1}{e_0} \iiint e^{i\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV \quad (\text{scattering amplitude})$$

$$\approx -\frac{1}{e_0} \iiint_{\text{cloud}} e^{i\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV \quad (\rho \sim 0 \text{ outside } e^- \text{ cloud})$$

$$\approx -\frac{1}{e_0} \iiint_{\text{cloud}} \rho(\mathbf{r}) dV \quad (\text{for } \mathbf{K} \cdot \mathbf{r} \ll 1 \text{ in } e^- \text{ cloud})$$

$$\sim Z_j \quad (\text{using } \iiint_{\text{cloud}} \rho dV \sim -Ze_0)$$

## Free Electrons

### Sommerfeld Free Electron Theory

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

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

$$\psi_{\mathbf{k}} = A e^{i\mathbf{k} \cdot \mathbf{r}} \quad (\text{ansatz for electron eigenfunctions})$$

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

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

### 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  $\hat{x}, \hat{y}, \hat{z}$  Cartesian directions, respectively.

$$V = L_x L_y L_z \quad (\text{crystal volume})$$

$$\Rightarrow \psi_{\mathbf{k}}(\mathbf{r}) = A e^{i\mathbf{k} \cdot \mathbf{r}} \rightarrow \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (A = \frac{1}{\sqrt{V}} \text{ for normalization})$$

### Periodic Boundary Conditions

Concept:  $e^-$  is confined to crystal interior (and not all space).

Boundary conditions on the electron wave function  $\psi$  must reflect this confinement.

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

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

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

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

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

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

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

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

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

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

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

### Quantization of $\mathbf{k}$ 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  $2\pi/L$ .

$$V_0^* = \frac{(2\pi)^3}{L^3} = \frac{8\pi^3}{V} \quad (\text{spacing btwn. allowed values of } \mathbf{k})$$

Consider a region of  $\mathbf{k}$  space with volume  $\Omega \gg V_0^*$ .

Concept: the number  $N_{\mathbf{k}}$  of allowed  $\mathbf{k}$  in  $\Omega$  will equal the volume of  $\Omega$  divided by the volume  $V_0^*$  around a single  $\mathbf{k}$  point.

$$N_{\mathbf{k}} = \frac{\Omega}{V_0^*} = \frac{\Omega V}{8\pi^3} \quad (\text{number of discrete } \mathbf{k} \text{ in } \Omega)$$

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

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

### Interpreting $\mathbf{k}$ as Free Electron Momentum

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (\text{review: electron wave function})$$

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

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

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

$\Rightarrow \hbar \mathbf{k}$  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.

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

### Fermi Sphere

Consider the  $T = 0$  K ground state of  $N$  free electrons

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

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

$\Rightarrow e^-$  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  $T = 0$  K.

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

The Fermi sphere's radius  $k_F$  defines the following...

$$V_F^* \equiv \frac{4\pi}{3} k_F^3 \quad (\text{volume of Fermi sphere})$$

$$E_F \equiv \frac{\hbar^2 k_F^2}{2m} \quad (\text{Fermi energy})$$

$$T_F \equiv \frac{E_F}{k_B} \quad (\text{Fermi temperature})$$

$$v_F \equiv \frac{\hbar k_F}{m} \quad (\text{Fermi velocity})$$

### 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.

$$V_F^* = \frac{4\pi}{3} k_F^3 \quad (\text{volume of Fermi sphere})$$

$$V_0^* = \frac{(2\pi)^3}{L^3} = \frac{(2\pi)^3}{V} \quad (\text{spacing btwn. discrete } \mathbf{k} \text{ states})$$

To determine  $N_e$ , consider the following...

- The  $\mathbf{k}$ -space volume of one allowed  $\mathbf{k}$  is  $V_0^* = \frac{(2\pi)^3}{V}$
- 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.

$\Rightarrow$  number of occupied free  $e^-$  levels in the ground state will equal total  $\mathbf{k}$ -space volume  $V_F^*$ , divided by  $V_0^*$ , times 2.

$$N_e = 2 \cdot \frac{V_F^*}{V_0^*} \quad (\text{factor of 2 from } e^- \text{ spin})$$

$$= \frac{k_F^3}{3\pi^2} V \quad (\text{number of occupied free } e^- \text{ levels})$$

$$k_F^3 = 3\pi^2 \frac{N_e}{V} \quad (\text{useful rearrangement})$$

$$n_e = \frac{N_e}{V} = \frac{k_F^3}{3\pi^2} \quad (\text{volume density of free } e^- \text{ levels})$$

## Density of Levels

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

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad (\text{review: Fermi energy})$$

$$N_e = \frac{k_F^3}{3\pi^2} \quad (\text{review: number of } e^- \text{ levels})$$

$$= \frac{V}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E_F^{3/2} \quad (\text{in terms of } E_F)$$

$$\rightarrow \frac{V}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{3/2} \quad (\text{generalizing } E_F \rightarrow E)$$

$$\mathcal{D}(E) \equiv \frac{dN_e}{dE} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \quad (\text{density of levels})$$

Interpretation: Density of levels  $\mathcal{D}$  (units energy<sup>-1</sup>) 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  $\mu$  in thermodynamic equilibrium at temperature  $T$ .

Chemical potential  $\mu$  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.

$$\beta \equiv \frac{1}{k_B T} \quad (\text{thermodynamic beta})$$

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

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

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

## TODO: Chemical Potential and Fermi Energy

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

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

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

$$E_F = \lim_{T \rightarrow 0 \text{ K}} \mu(T) \quad (\text{in a free electron gas})$$

## 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  $f(E)$ .

$$N_e = \int_0^\infty f(E) \mathcal{D}(E) dE \quad (\text{number of occupied } e^- \text{ states})$$

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.

$$N_e = \int_0^{E_F} \mathcal{D}(E) dE \quad (\text{at } T = 0 \text{ K})$$

## Volume-Normalized Density of Levels

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

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

Interpretation: volume-normalized density of levels (units energy<sup>-1</sup> volume<sup>-1</sup>) 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

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad (\text{review: Fermi energy})$$

$$k_F^3 = 3\pi^2 \frac{N_e}{V} \quad (\text{review: relating } k_F \text{ and } N_e)$$

$$\left( \frac{2m}{\hbar^2} \right)^{3/2} = \frac{N_e}{V} \frac{3\pi^2}{E_F^{3/2}} \quad (\text{combined and rearranged})$$

$$\text{Let } n_e \equiv \frac{N_e}{V} \quad (\text{volume density of occupied } e^- \text{ levels})$$

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

$$= \frac{3}{2} \frac{N_e}{E_F} \sqrt{\frac{E}{E_F}} \quad (\text{using above identity})$$

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

$$= \frac{3}{2} \frac{n_e}{E_F} \sqrt{\frac{E}{E_F}} \quad (\text{using } g = \frac{\mathcal{D}}{V} \text{ and } n_e = \frac{N_e}{V})$$

## Technique: Approximating Sums over $\mathbf{k}$ 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.

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

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

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

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

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

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

## Technique: Simplifying Integrals with $g(E)$

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

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

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

## Derivation

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

$$\Rightarrow \sqrt{E} = \frac{\hbar k}{\sqrt{2m}} \text{ and } dE = \frac{\hbar^2 k}{m} dk$$

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

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

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

$$= \frac{k^2}{\pi^2} dk \quad (\text{after simplifying})$$

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

## Average Internal Energy

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

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

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...

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

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

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

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



$$\langle u \rangle \approx \int_0^\infty f(E)g(E)E dE \quad (\text{free } e^- \text{ internal energy})$$

### Internal Energy at Zero Kelvin

$$\langle u \rangle \approx \int_0^\infty f(E)g(E)E dE \quad (\text{in general})$$

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

$$g(E) = \frac{3}{2} \frac{n_e}{E_F} \sqrt{\frac{E}{E_F}} \quad (\text{review: expression for } g(E))$$

$$\begin{aligned} \lim_{T \rightarrow 0 \text{ K}} \langle u \rangle &= \int_0^{E_F} E g(E) dE \\ &= \int_0^{E_F} E \cdot \frac{3}{2} \frac{n_e}{E_F} \sqrt{\frac{E}{E_F}} dE \quad (\text{substituting in } g(E)) \\ &= \frac{3}{5} n_e E_F \quad (\text{internal energy at zero kelvin}) \end{aligned}$$

### 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  $\mu$ . Without derivation, the *Sommerfeld expansion* of  $H(E)$  is for small temperatures  $T < T_F$  is...

$$\int_{-\infty}^\infty f(E)H(E) dE = \int_{-\infty}^\mu H(E) dE + \frac{\pi^2}{6} (k_B T)^2 \frac{dH}{dE} \Big|_{E=\mu} + \mathcal{O}(k_B T)^4$$

### Conservation of Electron Number

Important concept: the total number of electrons in a crystal is constant  $\Rightarrow N_e \neq N_e(T)$

$$N_e(T)|_{T=0} = N_e(T)|_{T>0}$$

$$n_e(T)|_{T=0} = n_e(T)|_{T>0}$$

$$n_e = \int_0^\infty f(E)g(E) dE \quad (\text{in general})$$

$$n_e = \int_0^{E_F} g(E) dE \quad (\text{at } T = 0 \text{ K})$$

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

$$\Rightarrow \int_0^\infty f(E)g(E) dE = \int_0^{E_F} g(E) dE \quad (\text{since } n_e \neq n_e(T))$$

### Sommerfeld Expansion of Electron Number Density

$$n_e = \int_0^\infty f(E)g(E) dE \quad (\text{in general})$$

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

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

### Sommerfeld Expansion of Chemical Potential

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

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

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

To proceed, we make the following approximations...

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

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

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

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

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

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

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

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

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

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

### Sommerfeld Expansion of Internal Energy

$$\langle u \rangle = \int_0^\infty f(E)g(E)E dE \quad (\text{in general})$$

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

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

$$\begin{aligned} u(T) &\approx \int_0^\mu g(E)E dE + \frac{\pi^2}{6} (k_B T)^2 \frac{d}{dE} [Eg(E)] \Big|_{E=\mu} \\ &= \int_0^\mu g(E)E dE + \frac{\pi^2}{6} (k_B T)^2 [g(\mu) + \mu g'(\mu)] \end{aligned}$$

$$\begin{aligned} &= \int_0^{E_F} g(E)E dE + \int_{E_F}^\mu g(E)E dE \quad (\text{splitting integral}) \\ &\quad + \frac{\pi^2}{6} (k_B T)^2 [g(\mu) + \mu g'(\mu)] \end{aligned}$$

To proceed, we make the following approximations...

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

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

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

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

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

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

From the Sommerfeld of chemical potential recall...

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

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

### Sommerfeld Expansion of Heat Capacity

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

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

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

$$g(E_F) = \frac{3}{2} \frac{n_e}{E_F} \quad (\text{TODO: reference})$$

$$\begin{aligned} \Rightarrow c_V &= \frac{\pi^2}{2} \frac{n_e}{E_F} k_B^2 T \quad (\text{Sommerfeld expansion of } c_V) \\ &= \frac{\pi^2}{2} n_e k_B \frac{T}{T_F} \quad (\text{in terms of } T_F) \end{aligned}$$

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

### In Passing: Molar Heat Capacity

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

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

$N_A$  is Avogadro's constant

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

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

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

## 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  $\tau$ . 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  $\mathcal{E}(t) = \mathcal{E}_0 e^{-i\omega t}$ .

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

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

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

$$\mathbf{r}_0 = \frac{e_0 \mathcal{E}_0}{m\omega^2 + i m \omega / \tau} \quad (\text{corresponding amplitude})$$

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

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

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

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

$$= \frac{n_e e_0^2 \mathcal{E}(t)}{m/\tau - i m \omega} \quad (\text{recognizing } \mathcal{E}(t))$$

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

### Conductivity in an Alternating Electric Field

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

$$\begin{aligned} \mathbf{j}(t) &= \frac{n_e e_0^2 \tau}{m} \frac{\mathcal{E}(t)}{1 - i\omega\tau} & (\text{review: current density in AC field}) \\ \mathbf{j} &= \sigma_E \mathcal{E} & (\text{Ohm's law in general}) \end{aligned}$$

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

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

### Conductivity in a Steady DC Electric Field

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

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

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

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

$$\mathbf{j} = -ne_0 \dot{\mathbf{r}} \quad (\text{current density in general})$$

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

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

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

$$\sigma_E = \frac{n_e e_0^2 \tau}{m} \quad (\text{result: conductivity in steady DC field})$$

### Shift of Fermi Sphere

Review: electron levels in a free electron gas at  $T = 0$  K are occupied up to the Fermi wave vector  $k_F$

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

$$\frac{d\mathbf{p}}{dt} = -e_0 \mathcal{E} \quad (\text{Newton's law for a free electron})$$

$$\hbar \frac{d\mathbf{k}}{dt} = -e_0 \mathcal{E} \quad (\text{using } \mathbf{p} = \hbar \mathbf{k} \text{ for free electrons})$$

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

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

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

### In Passing: Mean Free Path

$$v_F = \frac{\hbar k_F}{m} \quad (\text{Fermi velocity})$$

$$\ell \sim v_F \tau \quad (\text{estimate for mean free path})$$

Interpretation:  $\ell$  is the average distance traveled between collisions by electrons near the Fermi surface

Experimental values in copper assuming  $v_F = 1.57 \cdot 10^6 \text{ m s}^{-1}$

Temperature $T$	Mean free time $\tau$	Mean free path $\ell$
4 K	$2 \cdot 10^{-9} \text{ s}$	0.3 cm
300 K	$2 \cdot 10^{-14} \text{ s}$	$3 \cdot 10^{-6} \text{ cm}$

## 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  $\Lambda$  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...

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

- $n$  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.

$$\mathbf{k} = \frac{n_x}{N_x} \mathbf{b}_x + \frac{n_y}{N_y} \mathbf{b}_y + \frac{n_z}{N_z} \mathbf{b}_z, \quad n_i \in \mathbb{Z} \quad (\text{PBC})$$

- $u_{n\mathbf{k}}$  is a function with periodicity of the crystal's Bravais lattice, i.e.

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \quad (u \text{ has period of BL})$$

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

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

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

$$= e^{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{R})} u_{n\mathbf{k}}(\mathbf{r}) \quad (\text{since } u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) \equiv u_{n\mathbf{k}}(\mathbf{r}))$$

$$= e^{i\mathbf{k} \cdot \mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (\text{rearranging})$$

$$= e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) \quad (\text{recognizing original } \psi_{n\mathbf{k}})$$

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  $\psi$  is a wave vector  $\mathbf{k}$  for which

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}) \quad \forall \mathbf{R} \in \Lambda \quad (\text{alternate Bloch's theorem})$$

### Proof of Bloch's Theorem Using Translation Operators

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

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}) \text{ for all } \mathbf{R} \in \Lambda \quad (\text{potential is periodic})$$

$$H = -\frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r}) \quad (\text{electron Hamiltonian})$$

$$H(\mathbf{r} + \mathbf{R}) = H(\mathbf{r}) \quad (\text{since } U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}))$$

### Hamiltonian and Translation Operator Commute

$$\mathbf{T}_R f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}) \quad (\text{def. of translation operator } \mathbf{T}_R)$$

$$\begin{aligned} \mathbf{T}_R H(\mathbf{r}) \psi &= H(\mathbf{r} + \mathbf{R}) \mathbf{T}_R \psi \\ &= H(\mathbf{r}) \mathbf{T}_R \psi & (\text{using } H(\mathbf{r} + \mathbf{R}) = H(\mathbf{r})) \end{aligned}$$

$$\Rightarrow \mathbf{T}_R H = H \mathbf{T}_R \quad (\mathbf{T}_R, H \text{ commute})$$

Result: since  $\mathbf{T}_R$  and  $H$  commute, eigenstates of  $H$  can be chosen to also be eigenstates of  $\mathbf{T}_R$ .

$$H\psi = E\psi \quad (\text{eigenvalue equation for } H)$$

$$\mathbf{T}_R \psi = c(\mathbf{R}) \psi \quad (\text{eigenvalue equation for } \mathbf{T}_R)$$

### Lemma For $\mathbf{T}_R$ Eigenvalues

$$\mathbf{T}_R \mathbf{T}_{R'} \psi(\mathbf{r}) = \mathbf{T}_{R'} \mathbf{T}_R \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R} + \mathbf{R}')$$

$$\Rightarrow \mathbf{T}_{R'} \mathbf{T}_R = \mathbf{T}_R \mathbf{T}_{R'} = \mathbf{T}_{R+R'}$$

$$\mathbf{T}_{R'} \mathbf{T}_R \psi = c(\mathbf{R}) \mathbf{T}_{R'} \psi = c(\mathbf{R}) c(\mathbf{R}') \psi \quad (\text{result I})$$

$$= \mathbf{T}_{R+R'} \psi \quad (\text{using } \mathbf{T}_{R'} \mathbf{T}_R = \mathbf{T}_{R+R'})$$

$$= c(\mathbf{R} + \mathbf{R}') \psi \quad (\text{result II})$$

$$\Rightarrow c(\mathbf{R}) c(\mathbf{R}') = c(\mathbf{R} + \mathbf{R}') \quad (\text{combining I and II})$$

### Completing the Proof

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad n_j \in \mathbb{Z} \quad (\text{review: general BL vector})$$

$$c(\mathbf{R} + \mathbf{R}') = c(\mathbf{R}) c(\mathbf{R}') \quad (\text{review: } \mathbf{T}_R \text{ eigenvalue identity})$$

Write translation operator eigenvalues for primitive vectors  $\{\mathbf{a}_j\}$  in the general form...

$$c(\mathbf{a}_j) = e^{2\pi i x_j}, \quad x_j \in \mathbb{C} \quad (\text{eigval. for primitive vectors})$$

$$c(\mathbf{R}) = c(n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) \quad (\text{substituting in } \mathbf{R})$$

$$= c(n_1 \mathbf{a}_1) c(n_2 \mathbf{a}_2) c(n_3 \mathbf{a}_3) \quad (\text{using } \mathbf{T}_R \text{ eigval identity})$$

$$= e^{2\pi i (n_1 x_1 + n_2 x_2 + n_3 x_3)} \quad (\text{using } c(\mathbf{a}_j) = e^{2\pi i x_j})$$

Next, consider an arbitrary RL vector of the form...

$$\mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3$$



$i\mathbf{k} \cdot \mathbf{R} = 2\pi i(n_1x_1 + n_2x_2 + n_3x_3)$  (using  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ )  
 Compare to  $c(\mathbf{R}) = e^{2\pi i(n_1x_1 + n_2x_2 + n_3x_3)}$  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 $\mathbf{k}$ 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 **TODO: reference...**

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....

$e^{iN_j \mathbf{k} \cdot \mathbf{a}_j} = 1$ ,  $j = x, y, z$

$\Rightarrow N_j \mathbf{k} \cdot \mathbf{a}_j = 2\pi m_j$ ,  $m_j \in \mathbb{Z}$  (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...

$2\pi m_j = N_j (\sum_i x_i \mathbf{b}_i) \cdot \mathbf{a}_j$   
 $= 2\pi N_j x_j$  (using  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ )

$\Rightarrow x_j = \frac{m_j}{N_j}$  (solving for  $x_j$ )

Substitute  $x_j = m_j/N_j$  into  $\mathbf{k} = \sum_j x_j \mathbf{b}_j$  to get...

$\mathbf{k} = \sum_j \frac{m_j}{N_j} \mathbf{b}_j$ ,  $m_j \in \mathbb{Z}$  (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.

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

$\Rightarrow$  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  $\mathbf{b}_j/N_j$ .

$\Delta \mathbf{k} = \left| \frac{\mathbf{b}_1}{N_1} \cdot \left( \frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right) \right|$  ( $\mathbf{k}$ -space volume per allowed  $\mathbf{k}$ )  
 $= \frac{1}{N} |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|$  (using  $N = N_1 N_2 N_3$ )

$= \frac{V_0^*}{N}$  (recognizing volume of RL primitive unit cell)

**TODO: change everywhere: use  $\Delta \mathbf{k}$  for  $\mathbf{k}$  space volume and  $V_0^*$  for RL PUC volume.**

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.

$N_{\mathbf{k}} = \frac{V_0^*}{\Delta \mathbf{k}} = N$  (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  $V_0^* = (2\pi)^3/V_0$ .

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

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

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

$\Delta \mathbf{k} = \frac{(2\pi)^3}{V}$  (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; see **TODO: reference**.

### Proof of Bloch's Theorem by Explicit Construction

Consider a crystal described by a Bravais lattice  $\Lambda$  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:

- $\psi$  satisfies periodic boundary conditions, i.e.  
 $\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r})$ ,  $i = 1, 2, 3$  ( $\psi$  obeys PBC)
- The potential  $U$  has the periodicity of the BL, i.e.  
 $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$  ( $U$  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  $\psi$  satisfies the crystal's PBC,  $\psi$  may be expanded over a basis of plane waves with Bloch wave vectors obeying the PBC, i.e.

$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}$ , (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

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

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

Conclusion: ansatz for  $U$  satisfies lattice periodicity.

#### Interpreting the Potential Ansatz

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

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

$U_{\mathbf{K}} = \frac{1}{V_0} \iiint_{\text{cell}} U(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} dV$  (Fourier components)  
 $V_0$  is the volume of a single unit cell

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

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

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

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

#### Solving the Schrödinger Equation I

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

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

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

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

Substitute ansatzes for  $\psi$  and  $U$  into Schrödinger eq. to get...

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

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

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

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

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

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

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

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

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

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

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

### 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  $\mathbf{r} = \mathbf{d}$

$$\begin{aligned} \iiint_V e^{i\mathbf{q} \cdot \mathbf{r}} dV &= \iiint_{V'} e^{i\mathbf{q} \cdot (\mathbf{r} + \mathbf{d})} dV \\ &= \iiint_{V'} e^{i\mathbf{q} \cdot (\mathbf{r} + \mathbf{d})} dV \quad (\text{by PBC imposed on } \mathbf{q}) \end{aligned}$$

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

$\Rightarrow$  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

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

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

$\Rightarrow$  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.

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

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

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

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

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

Interpretation: above result is a homogeneous system of coupled linear equations for the coefficients  $c_{\mathbf{q}}$  needed to find  $\psi$ , 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  $\infty$  (like a hydrogen atom's principal quantum number.)

The electron wave function ansatz thus simplifies to...

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

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

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...

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

## 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  $Q_n = Q_n(E_n(\mathbf{k}))$  be a function of electron energy

Let  $Q$  denote the weighted sum of  $Q_n$  over all electron levels...  
 $Q = 2 \sum_{n, \mathbf{K}} Q_n(E_n(\mathbf{k}))$  (factor of 2 from  $e^-$  spin)

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

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

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

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

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

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

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

### DOL in a Fixed Energy Band

$$\int g(E) Q(E) dE = \sum_n \iiint Q_n(E_n(\mathbf{k})) \frac{d^3 \mathbf{k}}{4\pi^3} \quad (\text{for review})$$

Comparing LHS and RHS of above equality motivates...

$$g(E) \equiv \sum_n g_n(E) \quad (\text{summed over energy bands})$$

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

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

### Proof:

Substitute  $g_n(E)$  into  $g(E)$  to get...

$$g(E) = \frac{1}{4\pi^3} \sum_n \iiint \delta(E - E_n(\mathbf{k})) d^3 \mathbf{k}$$

Substitute  $g(E)$  into integral definition of  $q$  to get...

$$q = \int g(E) Q(E) dE$$

$$= \int \left\{ \sum_n \left[ \iiint \delta(E - E_n(\mathbf{k})) \frac{d^3 \mathbf{k}}{4\pi^3} \right] Q(E) \right\} dE$$

$$= \sum_n \iiint \left[ \int \delta(E - E_n(\mathbf{k})) Q(E) dE \right] \frac{d^3 \mathbf{k}}{4\pi^3} \quad (\text{rearranged})$$

$$= \sum_n \iiint Q_n(E_n(\mathbf{k})) \frac{d^3 \mathbf{k}}{4\pi^3} \quad (\text{by def. of } \delta \text{ function})$$

... 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  $g_n(E)$

$$g_n(E) = \iiint \delta(E - E_n(\mathbf{k})) \frac{d^3 \mathbf{k}}{4\pi^3} \quad (\text{review: DOL in } n\text{-th band})$$

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 be written as a surface integral.

Combine above three ideas to write  $g_n(E) dE$  as...

$$\begin{aligned} g_n(E) dE &= \iint_{S_n(E)} \frac{\delta \mathbf{k}}{4\pi^3} \cdot d\mathbf{S} \\ &\equiv \iint_{S_n(E)} \frac{\delta \mathbf{k}_{\perp}}{4\pi^3} dS \end{aligned}$$

$\delta k_{\perp}$  is the component of  $\delta \mathbf{k}$  normal to the surface  $S_n(E)$   
 $dE = \nabla E_n(\mathbf{k}) \cdot \delta \mathbf{k}$  (the differential  $dE$  in general)  
Recall  $\nabla E_n(\mathbf{k})$  is normal to surfaces of constant  $E$  to get...  
 $dE = |\nabla E_n(\mathbf{k})| \delta k_{\perp}$  (evaluating dot product)  
 $\Rightarrow \delta k_{\perp} = \frac{dE}{|\nabla E_n(\mathbf{k})|}$  (solving for  $\delta k_{\perp}$ )

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, cancell  $dE$  from both sides to get...  
 $g_n(E) = \frac{1}{4\pi^3} \iint_{S_n(E)} \frac{dS}{|\nabla E_n(\mathbf{k})|}$  (**gen. DOL in  $n$ -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  
 $\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K}) \cdot \mathbf{r}}$  (NFEM ansatz)

Wave function coefficients  $c_{\mathbf{k}-\mathbf{K}}$  and energies  $E$  are found by solving the eigenvalue problem...

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

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

Shorthand: let  $E_{\mathbf{k}}^{(0)} \equiv \frac{\hbar^2}{2m} k^2$  (free electron energy)  
 $(E_{\mathbf{k}-\mathbf{K}}^{(0)} - E) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0$  (in terms of  $E_{\mathbf{k}}^{(0)}$ )

### Limit Case: Free Electrons

Goal: analyze the NFEM for completely free electrons.  
 $U_{\mathbf{K}} = 0$  for all  $\mathbf{K}$  (for free electrons with  $U(\mathbf{r}) = 0$ )  
 $(E_{\mathbf{k}-\mathbf{K}}^{(0)} - E) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0$  (in general)  
 $(E_{\mathbf{k}-\mathbf{K}}^{(0)} - E) c_{\mathbf{k}-\mathbf{K}} = 0$  (for free electrons)

Conclusion: In limit of free electrons, for each  $\mathbf{K}$ , either  
(a)  $E = E_{\mathbf{k}-\mathbf{K}}^{(0)}$  (Bloch  $e^-$  have free  $e^-$  energy)  
(b)  $c_{\mathbf{k}-\mathbf{K}} = 0$  (the level  $\mathbf{k} - \mathbf{K}$  doesn't contribute to  $\psi_{\mathbf{k}}$ )  
More so,  $E = E_{\mathbf{k}-\mathbf{K}}^{(0)}$  can occur...

- (a) for a single  $\mathbf{K} = \mathbf{K}_0$ , giving the non-degenerate solution  
 $E = E_{\mathbf{k}-\mathbf{K}_0}^{(0)}$  (energy)  
 $\psi_{\mathbf{k}} \propto e^{i(\mathbf{k}-\mathbf{K}_0) \cdot \mathbf{r}}$  (wave function)
- (b) for multiple  $\mathbf{K} = \mathbf{K}_1, \dots, \mathbf{K}_m$ , giving the degenerate solution  
 $E = E_{\mathbf{k}-\mathbf{K}_1} = \dots = E_{\mathbf{k}-\mathbf{K}_m}$  (energy)  
 $\psi_{\mathbf{k}} \propto a_1 e^{i(\mathbf{k}-\mathbf{K}_1) \cdot \mathbf{r}} + \dots + a_m e^{i(\mathbf{k}-\mathbf{K}_m) \cdot \mathbf{r}}$  (wave function)

### NFEM: Typical Analysis Procedure

1. Choose a fixed  $\mathbf{k}$  in the first Brillouin 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  
 $(E_{\mathbf{k}-\mathbf{K}}^{(0)} - E) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} = 0$

to get  $m$  eigenvalues  $\{E_{n\mathbf{k}}\}$  and eigenvectors  $\mathbf{c}_{\mathbf{k}}^{(n)} \in \mathbb{C}^m$   
 $\mathbf{c}_{\mathbf{k}}^{(n)} = (c_{\mathbf{k}-\mathbf{K}_1}^{(n)}, \dots, c_{\mathbf{k}-\mathbf{K}_m}^{(n)})$  (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...

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

## 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  $E = E_{\mathbf{k}-\mathbf{K}_0}^{(0)}$ .

$$E - E_{\mathbf{k}-\mathbf{K}_0}^{(0)} = 0 \quad (\text{free } e^- \text{ nondegenerate energy})$$

Concept: for a weak potential  $U(\mathbf{r})$ , the condition that  $E_{\mathbf{k}-\mathbf{K}}^{(0)}$  be nondegenerate generalizes to...

$$|E_{\mathbf{k}-\mathbf{K}}^{(0)} - E_{\mathbf{k}-\mathbf{K}_0}^{(0)}| \gg U_{\mathbf{K}'}, \text{ for all } \mathbf{K} \neq \mathbf{K}_0 \text{ and } U_{\mathbf{K}'}$$

Interpretation: the free electron energy  $E_{\mathbf{k}-\mathbf{K}_0}^{(0)}$  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  $E_{\mathbf{k}-\mathbf{K}_0}^{(0)}$ .

### Analysis

Consider the non-degenerate free  $e^-$  level  $E_{\mathbf{k}-\mathbf{K}_0}^{(0)}$ .

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K}) \cdot \mathbf{r}} \quad (\text{review: NFEM ansatz})$$

$$(E - E_{\mathbf{k}-\mathbf{K}}^{(0)}) c_{\mathbf{k}-\mathbf{K}} = \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} \quad (\text{review: NFEM eqs.})$$

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

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

**TODO: redo as for near-degenerate/as in Ashcroft.** Goal: find approximate expression for  $c_{\mathbf{k}-\mathbf{K}}$  for weak potential and non-degenerate level with  $\mathbf{K} = \mathbf{K}_0$ .

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

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

Substitute this sum into general NFEM system of eq. to get...

$$(E - E_{\mathbf{k}-\mathbf{K}'}^{(0)}) c_{\mathbf{k}-\mathbf{K}'} \approx c_{\mathbf{k}-\mathbf{K}_0} U_{\mathbf{K}_0-\mathbf{K}'} \quad (\text{for a ndg. level})$$

Solve for  $c_{\mathbf{k}-\mathbf{K}'}$  and reindex  $\mathbf{K}' \rightarrow \mathbf{K}$  to get...

$$\Rightarrow c_{\mathbf{k}-\mathbf{K}} \approx \frac{c_{\mathbf{k}-\mathbf{K}_0} U_{\mathbf{K}_0-\mathbf{K}}}{E - E_{\mathbf{k}-\mathbf{K}}^{(0)}} \quad (\text{result: } c_{\mathbf{k}} \text{ for ndg. level})$$

### Solving for Energy

Solve system of NFEM eqs. with chosen  $\mathbf{K} = \mathbf{K}_0$ , giving...

$$(E - E_{\mathbf{k}-\mathbf{K}_0}^{(0)}) c_{\mathbf{k}-\mathbf{K}_0} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_0} \quad (\text{for } \mathbf{K} = \mathbf{K}_0)$$

$$= \sum_{\mathbf{K} \neq \mathbf{K}_0} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_0} \quad (\text{since } U_0 = 0)$$

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

$$\approx \sum_{\mathbf{K} \neq \mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} |U_{\mathbf{K}-\mathbf{K}_0}|^2}{E - E_{\mathbf{k}-\mathbf{K}}^{(0)}} \quad (U_{\mathbf{K}}^* = U_{-\mathbf{K}})$$

$$E = E_{\mathbf{k}-\mathbf{K}_0}^{(0)} + \sum_{\mathbf{K} \neq \mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} |U_{\mathbf{K}-\mathbf{K}_0}|^2}{E - E_{\mathbf{k}-\mathbf{K}}^{(0)}} \quad (\text{solving for } E)$$

$$\approx E_{\mathbf{k}-\mathbf{K}_0}^{(0)} + \sum_{\mathbf{K} \neq \mathbf{K}_0} \frac{c_{\mathbf{k}-\mathbf{K}_0} |U_{\mathbf{K}-\mathbf{K}_0}|^2}{E_{\mathbf{k}-\mathbf{K}_0}^{(0)} - E_{\mathbf{k}-\mathbf{K}}^{(0)}} \quad (E \approx E_{\mathbf{k}-\mathbf{K}_0}^{(0)} \text{ in denom})$$

Conclusion: the NFEM corrections to a nondegenerate free electron level  $E_{\mathbf{k}-\mathbf{K}}^{(0)}$  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  $\mathbf{K}_1, \dots, \mathbf{K}_m$  with degenerate free electron energies

$$E - E_{\mathbf{k}-\mathbf{K}_i}^{(0)} = 0 \text{ for } i = 1, \dots, m$$

Concept: for a weak potential, the condition that the  $E_{\mathbf{k}-\mathbf{K}_i}^{(0)}$  be degenerate generalizes to the near-degeneracy condition

$$|E_{\mathbf{k}-\mathbf{K}}^{(0)} - E_{\mathbf{k}-\mathbf{K}_i}^{(0)}| \gg U_{\mathbf{K}'}, \text{ for all } \mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m, \text{ all } U_{\mathbf{K}'}, \text{ and } i = 1, \dots, m.$$

Interpretation: the free electron energies  $E_{\mathbf{k}-\mathbf{K}_i}^{(0)}$  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  $E_{\mathbf{k}-\mathbf{K}_i}^{(0)}$ ,  $i = 1, \dots, m$ .

### Approximate Expression for Coefficients

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

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

$$(E - E_{\mathbf{k}-\mathbf{K}}^{(0)}) c_{\mathbf{k}-\mathbf{K}} = \sum_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} \quad (\text{review: NFEM eqs.})$$

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

$$= \frac{1}{E - E_{\mathbf{k}-\mathbf{K}}^{(0)}} \left( \sum_{j=1}^m c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j-\mathbf{K}} + \sum_{\mathbf{K}' \neq \mathbf{K}_1, \dots, \mathbf{K}_m} c_{\mathbf{k}-\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} \right) \quad (\text{decomposing sum})$$

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

### Solving for Energy

Solve the system of NFEM equations. with the near-degenerate  $\mathbf{K} = \mathbf{K}_1, \dots, \mathbf{K}_m$ , giving...

$$(E - E_{\mathbf{k}-\mathbf{K}_i}^{(0)}) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_i}, \quad i = 1, \dots, m$$

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

$$+ \sum_{\mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m} c_{\mathbf{k}-\mathbf{K}} U_{\mathbf{K}-\mathbf{K}_i}$$

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

$c_{\mathbf{k}-\mathbf{K}})$

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

$$(E - E_{\mathbf{k}-\mathbf{K}_i}^{(0)}) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{j=1}^m c_{\mathbf{k}-\mathbf{K}_j} U_{\mathbf{K}_j-\mathbf{K}_i} + \dots$$

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

Conclusion: the NFEM corrections to a set of near-degenerate free electron levels  $E_{\mathbf{k}-\mathbf{K}_i}^{(0)}$  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...

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

### 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  $E_{\mathbf{k}-\mathbf{K}_i}^{(0)}$  given by...

$|E_{\mathbf{k}-\mathbf{K}}^{(0)} - E_{\mathbf{k}-\mathbf{K}_i}^{(0)}| \gg U_{\mathbf{K}'}$  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  $E_{\mathbf{k}-\mathbf{K}_i}^{(0)}$ ,  $i = 1, 2$ .

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

Use  $U_0$  and write out the two equations to get...

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

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

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

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

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

$$(E_{\mathbf{q}}^{(0)} - E) c_{\mathbf{q}} + c_{\mathbf{q}-\mathbf{K}} U_{\mathbf{K}} = 0 \quad (\text{for } i = 1)$$

$$(E_{\mathbf{q}-\mathbf{K}}^{(0)} - E) c_{\mathbf{q}-\mathbf{K}} + c_{\mathbf{q}} U_{-\mathbf{K}} = 0 \quad (\text{for } i = 2)$$

$$\begin{pmatrix} E_{\mathbf{q}}^{(0)} - E & U_{\mathbf{K}} \\ U_{\mathbf{K}}^* & E_{\mathbf{q}-\mathbf{K}}^{(0)} - E \end{pmatrix} \begin{pmatrix} c_{\mathbf{q}} \\ c_{\mathbf{q}-\mathbf{K}} \end{pmatrix} = \mathbf{0} \quad (\text{in matrix form})$$

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

$$\det \begin{pmatrix} E_{\mathbf{q}}^{(0)} - E & U_{\mathbf{K}} \\ U_{\mathbf{K}}^* & E_{\mathbf{q}-\mathbf{K}}^{(0)} - E \end{pmatrix} = 0$$

$$\Rightarrow E = \frac{1}{2} (E_{\mathbf{q}}^{(0)} + E_{\mathbf{q}-\mathbf{K}}^{(0)}) \pm \frac{1}{2} \sqrt{(E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}-\mathbf{K}}^{(0)})^2 + 4|U_{\mathbf{K}}|^2}$$

Interpretation:  $\frac{1}{2} (E_{\mathbf{q}}^{(0)} + E_{\mathbf{q}-\mathbf{K}}^{(0)}) = \frac{1}{2} (E_{\mathbf{k}-\mathbf{K}_1}^{(0)} + E_{\mathbf{k}-\mathbf{K}_2}^{(0)})$  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:  $E_{\mathbf{q}-\mathbf{K}}^{(0)} \approx E_{\mathbf{q}}^{(0)}$  and  $|E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}-\mathbf{K}}^{(0)}| \gg U_{\mathbf{K}''}$  for all  $\mathbf{K}' \neq \mathbf{K}$  and all  $U_{\mathbf{K}''}$ .

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

$$|\mathbf{q}| = |\mathbf{q} - \mathbf{K}| \quad (\text{for double degeneracy})$$

$$|\mathbf{q}|^2 = |\mathbf{q} - \mathbf{K}|^2 \quad (\text{squaring})$$

$$q^2 = q^2 - 2\mathbf{q} \cdot \mathbf{K} + K^2 \quad (\text{multiplying out})$$

$$\mathbf{q} \cdot \mathbf{K} = \frac{K^2}{2} \quad (\text{simplified and rearranged})$$

$$\mathbf{q} \cdot \hat{\mathbf{K}} = \frac{K}{2} \quad (\text{letting } \hat{\mathbf{K}} \equiv \mathbf{K}/|\mathbf{K}|)$$

Interpretation:  $\mathbf{q} \cdot \hat{\mathbf{K}} = K/2$  is the equation of Bragg plane defined by the reciprocal lattice vector  $\mathbf{K} \Rightarrow$  the degeneracy condition  $E_{\mathbf{q}}^{(0)} = E_{\mathbf{q}-\mathbf{K}}^{(0)}$  is satisfied for  $\mathbf{q}$  falling in the Bragg plane defined by  $\mathbf{K}$ .

**TODO: interpret:**

"The case of two near-degenerate levels applies to an electron whose wave vector very nearly satisfies the condition for a single Bragg scattering".

"A weak periodic potential has its major effects only on those free electron levels whose wave vectors are close to ones at which Bragg reflections can occur."

### Energy Gradient

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

$$E_{\mathbf{q}} = \frac{1}{2} (E_{\mathbf{q}}^{(0)} + E_{\mathbf{q}-\mathbf{K}}^{(0)}) \quad (\text{review: doubly-degenerate level})$$

$$\pm \frac{1}{2} \sqrt{(E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}-\mathbf{K}}^{(0)})^2 + 4|U_{\mathbf{K}}|^2}$$

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

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

$$\nabla_{\mathbf{q}} E_{\mathbf{q}} = \frac{\hbar^2}{4m} \nabla_{\mathbf{q}} (|\mathbf{q}|^2 + |\mathbf{q} - \mathbf{K}|^2) \quad (\text{at } E_{\mathbf{q}}^{(0)} = E_{\mathbf{q}-\mathbf{K}}^{(0)})$$

$$= \frac{1}{2} \frac{\hbar^2}{2m} \nabla_{\mathbf{q}} (2|\mathbf{q}|^2 - 2\mathbf{q} \cdot \mathbf{K} + |\mathbf{K}|^2) \quad (\text{multiplying out})$$

$$= \frac{\hbar^2}{4m} (4\mathbf{q} - 2\mathbf{K} + \mathbf{0}) \quad (\text{evaluating gradient})$$

$$= \frac{\hbar^2}{m} (\mathbf{q} - \frac{\mathbf{K}}{2}) \quad (\text{simplifying})$$

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  $E_{\mathbf{q}} \Rightarrow$  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.

$$U_{\text{at}} = -\frac{e_0^2}{4\pi\epsilon_0 r} \quad (\text{the atomic sytem's Coulomb potential})$$

$$\mu = \frac{mM}{m+M} \approx m \quad (\text{reduced mass})$$

$$H_{\text{at}} = -\frac{\hbar^2}{2\mu} \nabla^2 - U_{\text{at}} \quad (\text{system's Hamiltonian})$$

$$\approx -\frac{\hbar^2}{2m} \nabla^2 - \frac{e_0^2}{4\pi\epsilon r} \quad (\text{since } \mu \approx m)$$

$$H_{\text{at}} \psi_{nlm_l} = E_{nlm_l} \psi_{nlm_l} \quad (\text{electron Schrödinger equation})$$

$\psi_{nlm_l}$  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)

$$H_{\text{at}} \psi_\nu = E_\nu \psi_\nu \quad (e^- \text{ Schrödinger eq. in terms of } \nu)$$

## 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.

$$U_{\text{at}}(\mathbf{r}) = -\frac{e_0^2}{4\pi\epsilon_0 r} \quad (\text{a single atom's potential})$$

$$U_{\text{lattice}}(\mathbf{r}) = \sum_{\mathbf{R}} U_{\text{at}}(\mathbf{r} - \mathbf{R}) \quad (\text{the lattice's potential})$$

$$\Delta U \equiv \sum_{\mathbf{R} \neq \mathbf{0}} U_{\text{at}}(\mathbf{r} - \mathbf{R}) \quad (\text{lattice potential minus origin atom})$$

$$H_{\text{at}} = -\frac{\hbar^2}{2m} \nabla^2 + U_{\text{at}}(\mathbf{r}) \quad (\text{for isolated atom at origin})$$

$$H = H_{\text{at}} + \Delta U, \quad (\text{for atom at origin plus lattice})$$

$$\approx H_{\text{at}} \quad (\text{near origin atom})$$

## TBM Ansatz for Bloch Electrons

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

$\psi_\nu$  are isolated atomic eigenfunctions

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi(\mathbf{r} - \mathbf{R}) \quad (\text{TBM ansatz for Bloch } e^-)$$

$$\phi(\mathbf{r}) = \sum_{\nu} b_\nu \psi_\nu(\mathbf{r}) \quad (\text{TBM basis function})$$

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  $\psi(\mathbf{r})$ .

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

Take scalar product with arbitrary atomic eigenfun.  $\psi_\mu$  to get...

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

$$\iiint \psi_\mu^* H_{\text{at}} \psi \, dV = E_\mu \iiint \psi_\mu^* \psi \, dV \quad (\text{using } H_{\text{at}} \psi_\mu = E_\mu \psi_\mu)$$

Substitute TBM ansatz for  $\psi$  into scalar product to get...

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

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

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

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

## Summarizing Results So Far

$$\iiint \psi_\mu^* H \psi \, dV = E_\mu \iiint \psi_\mu^* \psi \, dV \quad (\text{i})$$

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

## TBM: Solving the Schrödinger Equation II

Continue with scalar product of Schrödinger eq. with  $\psi_\mu^*$ , 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..

$$(E - E_\mu) \iiint \psi_\mu^* \psi \, dV = \iiint \psi_\mu^* \Delta U \psi \, dV \quad (\text{using result (i)})$$

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

Finally, substitute ansatz for  $\psi$  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...

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

Interpretation: in principle, this result is a system of equations for the coefficients  $b_\nu$  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.

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

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

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

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

Use the above simplifications to make the approximation...

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

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 ( $l = 0, m_l = 0$ )

$$b_\nu \approx \begin{cases} b_s & \nu \text{ is an } s \text{ orbital} \\ 0 & \text{otherwise} \end{cases} \quad (\text{consider only } s \text{ orbital})$$

$$\sum_{\nu} b_\nu \approx b_s \quad (\text{neglecting other orbitals})$$

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

$$\dots = \sum_{\nu} b_\nu \iiint \psi_\mu^* \Delta U(\mathbf{r}) \psi_\nu(\mathbf{r}) \, dV + \dots \quad (\text{general TBM eqs.})$$

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

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

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

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  $\alpha, \beta, \gamma$ , 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...

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

## In Practice:

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

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

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



# 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  $\mathbf{k}$

$$\psi_{\mathbf{k}}(\mathbf{r}) \propto e^{i\mathbf{k} \cdot \mathbf{r}} \quad (\text{free electron wave function})$$

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

$$\mathbf{p} = \hbar \mathbf{k} \quad (\text{free electron momentum})$$

$$\mathbf{v} = \frac{\hbar \mathbf{k}}{m} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}) \quad (\text{free electron velocity})$$

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  $n$

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

$u_{n\mathbf{k}}$  is a periodic function with period of the underlying Bravais lattice  $\Lambda$ , 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...

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_n(\mathbf{k}) \quad (\text{velocity of Bloch electron})$$

- (iv) The dynamics of a Bloch electron are governed by...

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

## Electron Dynamics: Informal Derivation

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

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

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

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

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

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

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

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

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

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

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

## Bloch Electron in a Magnetic Field

Consider Bloch electron in a homogeneous magnetic field

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

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

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

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

$$[\mathbf{v}_n(\mathbf{k}) \times \mathbf{B}]_z = 0 \Rightarrow \frac{dk_z}{dt} = 0 \quad (\text{for } \mathbf{B} = B_0 \hat{\mathbf{e}}_z)$$

$$\Rightarrow k_z \text{ is a constant of motion in a homog. magnetic field}$$

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

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

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

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

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  $\mathcal{E}(\mathbf{r}, t) = \mathcal{E}_0$  and no external magnetic field.

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

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

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

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  $\gamma$

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

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

$$E(k) = -\gamma \cos(ka) \quad (\text{see "TBM and the } s \text{ Orbital"})$$

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

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

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

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

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

Consider one period  $t_B$  of a Bloch oscillation...

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

$$\Rightarrow t_B = \frac{2\pi \hbar}{e_0 a \mathcal{E}} \quad (\text{solving for } t_B)$$

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

$$= \frac{\gamma k}{\hbar} \sin(ka) \quad (\text{differentiating})$$

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

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

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

## In Passing: Validity of Semiclassical Equations

Consider electrons in the  $n$ -th band of a material with Fermi energy  $E_F$  and band gap  $E_{\text{gap}}$  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...

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

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

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

$$E_F \sim 1 \text{ eV to } 10 \text{ eV in metals}$$

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

$$\Rightarrow ae_0 \mathcal{E} \sim 10^{-10} \text{ eV} \ll \frac{E_{\text{gap}}^2}{E_F} \sim 0.1 \text{ eV}$$

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  $\mu(T) - E_n(\mathbf{k}) \gg k_B T$ , so that  $f(E_n(\mathbf{k})) \approx 1$  for all  $\mathbf{k}$  in the band.

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

$\mu - E_n(\mathbf{k}) \gg k_B T$  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 interband transitions.

## Electron Current in Filled Bands

Goal: generalize the free electron expression  $\mathbf{j}_{el} = -n_e e_0 \mathbf{v}$  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.

$\mathbf{j}_{el}^{(n)} = -e_0 \iiint_{\text{BZ}} \mathbf{v}_n(\mathbf{k}) \frac{d^3 \mathbf{k}}{4\pi^3}$  (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  $\mathbf{j}_{el} = n_e E \mathbf{v}$  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)

$= \frac{1}{\hbar} \iiint E_n(\mathbf{k}) \nabla_{\mathbf{k}} E_n(\mathbf{k}) \frac{d^3 \mathbf{k}}{4\pi^3}$  (in terms of  $E_n(\mathbf{k})$ )

$= \frac{1}{2\hbar} \iiint \nabla_{\mathbf{k}} [E_n(\mathbf{k})^2] \frac{d^3 \mathbf{k}}{4\pi^3}$  (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  $[E_n(\mathbf{k})]^2$  are periodic over the first Brillouin zone. The integral of a periodic function over one period is zero, so the integrals in both  $\mathbf{j}_n^{(el)}$  and  $\mathbf{j}_n^{(E)}$  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 determining a solid's insulating properties.

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

$\Rightarrow$  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 Brillouin 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

**TODO: just add more explanation in words.**

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

Review: filled bands cannot carry current.

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

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

$$\begin{aligned} \mathbf{j}_{\text{full}} &= -e_0 \iiint_{\text{BZ}} \mathbf{v} \frac{d^3 \mathbf{k}}{4\pi^3} = \mathbf{0} \\ &= -e_0 \iiint_{\text{occupied}} \mathbf{v} \frac{d^3 \mathbf{k}}{4\pi^3} + (-e_0) \iiint_{\text{empty}} \mathbf{v} \frac{d^3 \mathbf{k}}{4\pi^3} = \mathbf{0} \\ \Rightarrow &(-e_0) \iiint_{\text{occupied}} \mathbf{v} \frac{d^3 \mathbf{k}}{4\pi^3} = (+e_0) \iiint_{\text{empty}} \mathbf{v} \frac{d^3 \mathbf{k}}{4\pi^3} \end{aligned}$$

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  $\mathbf{m}$  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...

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

## Review: Free Electron Dispersion

$E_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$  (free electron dispersion)

$$\Rightarrow \frac{2E_0}{\hbar^2 k^2} = \frac{1}{m} = \frac{1}{\hbar^2} \frac{\partial^2 E_0}{\partial k^2}$$

$$\Rightarrow m^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \quad (\text{for free electrons})$$

$$E_0(\mathbf{k}) = \frac{1}{2\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \cdot (\hbar^2 k^2) \quad (\text{in terms of above } 1/m)$$

## Introducing the Effective Mass Tensor

$E_n(\mathbf{k}) \approx E_n(\mathbf{k}_0) + \frac{1}{2} \left. \frac{\partial^2 E_n}{\partial k_i \partial k_j} \right|_{\mathbf{k}_0} \delta k_i \delta k_j$  (Bloch electrons)

$E_0(\mathbf{k}) = \frac{1}{2\hbar^2} \frac{\partial^2 E_0}{\partial k^2} \cdot (\hbar^2 k^2)$  (free electrons)

$m^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E_0}{\partial k^2}$  (free electrons)

Comparing expressions for free and Bloch electrons motivates the definition of an effective mass tensor  $\mathbf{m}$  according to...

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

Plus sign corresponds to effective mass of electrons

Minus sign corresponds to effective mass of holes

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

## Effective Mass Tensor in Terms of Velocity

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

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

$[\mathbf{v}_n(\mathbf{k})]_i = \frac{1}{\hbar} \frac{\partial}{\partial k_i} E_n(\mathbf{k})$  (by components)

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

$$[\mathbf{m}_n^{-1}(\mathbf{k})]_{ij} = \pm \frac{1}{\hbar} \frac{\partial}{\partial k_j} [\mathbf{v}_n(\mathbf{k})]_i \quad (\text{in terms of } \mathbf{v}_n)$$

$$\mathbf{m}_n^{-1}(\mathbf{k}) = \pm \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{v}_n(\mathbf{k}) \quad (\text{in vector form})$$

## Dynamics in Terms of Effective Mass Tensor

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

$\mathbf{m}_n^{-1}(\mathbf{k}) = \pm \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{v}_n(\mathbf{k})$  (review:  $\mathbf{m}$  in terms of  $\mathbf{v}_n(\mathbf{k})$ )

$\mathbf{a}_n = \frac{d\mathbf{v}_n(\mathbf{k})}{dt}$  (acceleration of Bloch electron)

$$= \nabla_{\mathbf{k}} \mathbf{v}_n(\mathbf{k}) \cdot \frac{d\mathbf{k}}{dt} \quad (\text{using the chain rule})$$

$$= \pm \hbar \mathbf{m}_n^{-1} \frac{d\mathbf{k}}{dt} \quad (\text{using } \mathbf{m}^{-1} = \pm \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{v})$$

$$\mathbf{m}_n \mathbf{a}_n = \pm \hbar \frac{d\mathbf{k}}{dt} \quad (\text{rearranged})$$

$$= \mp e_0 (\mathcal{E} + \mathbf{v}_n \times \mathbf{B}) \quad (\text{result: dynamics in terms of } \mathbf{m})$$

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  $\mathbf{k} = \mathbf{0}$ .

$$E_{cb}(\mathbf{k}) = E_c + \frac{\hbar^2}{2} k_i (m_c)^{-1} k_j \quad (\text{conduction band dispersion})$$

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

$$m_c = \begin{pmatrix} m_{c1}^* & 0 & 0 \\ 0 & m_{c2}^* & 0 \\ 0 & 0 & m_{c3}^* \end{pmatrix} \quad (\text{in system of principle axes})$$

$$m_c^{-1} = \begin{pmatrix} \frac{1}{m_{c1}^*} & 0 & 0 \\ 0 & \frac{1}{m_{c2}^*} & 0 \\ 0 & 0 & \frac{1}{m_{c3}^*} \end{pmatrix} \quad (\text{in system of principle axes})$$

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

$$E_{cb}(\mathbf{k}) = E_c + \frac{\hbar^2}{2} \left( \frac{k_1^2}{m_{c1}^*} + \frac{k_2^2}{m_{c2}^*} + \frac{k_3^2}{m_{c3}^*} \right) \quad (\text{in system of PA})$$

### 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  $\mathbf{k} = \mathbf{0}$ .

$$E_{vb}(\mathbf{k}) = E_v - \frac{\hbar^2}{2} k_i (m_v)^{-1} k_j \quad (\text{valence band dispersion})$$

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

$$m_v = \begin{pmatrix} m_{v1}^* & 0 & 0 \\ 0 & m_{v2}^* & 0 \\ 0 & 0 & m_{v3}^* \end{pmatrix} \quad (\text{in system of principle axes})$$

$$m_v^{-1} = \begin{pmatrix} \frac{1}{m_{v1}^*} & 0 & 0 \\ 0 & \frac{1}{m_{v2}^*} & 0 \\ 0 & 0 & \frac{1}{m_{v3}^*} \end{pmatrix} \quad (\text{in system of principle axes})$$

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

$$E_{vb}(\mathbf{k}) = E_v - \frac{\hbar^2}{2} \left( \frac{k_1^2}{m_{v1}^*} + \frac{k_2^2}{m_{v2}^*} + \frac{k_3^2}{m_{v3}^*} \right) \quad (\text{in system of PA})$$

## 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 determining a solid's insulating properties.

⇒ Materials with only full ground-state bands are insulators.

⇒ 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  $T > 0$  K (but below the material's melting point).

$$E_g \lesssim 1 \text{ eV} \quad (\text{typical semiconductor band gap})$$

$$E_g \gtrsim 5 \text{ eV} \quad (\text{typical insulator band gap})$$

$$k_B T \sim 0.025 \text{ eV at } T \sim 300 \text{ K} \quad (\text{for reference})$$

### 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.

- TODO: homogeneous
- TODO: inhomogeneous

## Homogeneous Semiconductors

TODO: homogeneous semiconductors are...

### 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

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

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

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

### 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

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

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

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

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

$$= \int_{-\infty}^{E_v} g_v(E) [1 - f(E)] dE \quad (\text{VB occupied only up to } E_v)$$

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

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

$$E_c > \mu \quad (\text{follows from requiring } n_c \rightarrow 0 \text{ as } T \rightarrow 0 \text{ K})$$

$$E_v < \mu \quad (\text{follows from requiring } p_v \rightarrow 0 \text{ as } T \rightarrow 0 \text{ K})$$

$$\Rightarrow E_v < \mu < E_c \quad (\text{chemical potential lies in band gap})$$

### Non-Degenerate Semiconductor Approximation

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

$$E_c - \mu \gg k_B T \quad (\text{non-degenerate SC approximation})$$

$$\mu - E_v \gg k_B T \quad (\text{non-degenerate SC approximation})$$

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.

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

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

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

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

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

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

### Hole Density in the Non-Degenerate SC Approx.

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

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

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

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

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

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

### Conduction and Valence Band Dispersion Relatins

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

- (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**”

$$E_{cb}(\mathbf{k}) = E_c + \frac{\hbar^2}{2} k_i (m_c^*)^{-1} k_j \quad (\text{conduction band dispersion})$$

$$= E_c + \frac{\hbar^2}{2} \left( \frac{k_1^2}{m_{c1}^*} + \frac{k_2^2}{m_{c2}^*} + \frac{k_3^2}{m_{c3}^*} \right) \quad (\text{in m's system of PA})$$

$$= E_c + \frac{\hbar^2 k^2}{2m_c^*} \quad (\text{assuming three equal eigenvalues})$$

$$E_{vb}(\mathbf{k}) = E_v - \frac{\hbar^2}{2} k_i (m_v^*)^{-1} k_j \quad (\text{valence band dispersion})$$

$$= E_v - \frac{\hbar^2}{2} \left( \frac{k_1^2}{m_{v1}^*} + \frac{k_2^2}{m_{v2}^*} + \frac{k_3^2}{m_{v3}^*} \right) \quad (\text{in m's system of PA})$$

$$= E_v - \frac{\hbar^2 k^2}{2m_v^*} \quad (\text{assuming three equal eigenvalues})$$

**TODO:** clarify  $\mathbf{k}$ -space position of extrema e.g. at  $\mathbf{k}_0$  and adjust expansions accordingly.

#### Expressions for Densities of State

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

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

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

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

- (i) shift in energy by  $E_c$  or  $E_v$
  - (ii) electron  $m$  replaced by  $m_c^*$  or  $m_v^*$
- $\Rightarrow$  we find the CB and VB densities of state by shifting the free  $e^-$  DOS by  $E_c$  or  $E_v$  and replacing  $m$  with  $m_c^*$  or  $m_v^*$ .

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

$$g_c(E) = \frac{1}{2\pi^2} \left( \frac{2m_c^*}{\hbar^2} \right)^{3/2} \sqrt{|E_c - E|} \quad (\text{CB density of state})$$

$$g_v(E) = \frac{1}{2\pi^2} \left( \frac{2m_v^*}{\hbar^2} \right)^{3/2} \sqrt{|E_v - E|} \quad (\text{VB density of state})$$

Note: for an effective mass tensor with different eigenvalues  $m_1^*, m_2^*, m_3^*$ , replace  $m_c^*$  or  $m_v^*$  with...

$$(m_c^*)^{3/2} \rightarrow (m_{c1}^*, m_{c2}^*, m_{c3}^*) \quad (\text{for } m_c \text{ with different eigvals.})$$

$$(m_v^*)^{3/2} \rightarrow (m_{v1}^*, m_{v2}^*, m_{v3}^*) \quad (\text{for } m_v \text{ with different eigvals.})$$

#### Evaluating $N_c$

$$N_c(T) = \int_{E_c}^{\infty} g_c(E) e^{-\beta(E-E_c)} dE \quad (\text{from above})$$

$$= \frac{1}{2\pi^2} \left( \frac{2m_c^*}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} e^{-\beta(E-E_c)} \sqrt{|E_c - E|} dE$$

Let  $x \equiv \beta(E - E_c)$  (new integration variable)

$$N_c(T) = \frac{\sqrt{2}}{\pi^2} \left( \frac{m_c^* k_B T}{\hbar^2} \right)^{3/2} \int_0^{\infty} \sqrt{x} e^{-x} dx \quad (\text{in terms of } x)$$

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

$$N_c(T) = \frac{1}{4} \left( \frac{2m_c^* k_B T}{\pi \hbar^2} \right)^{3/2} \quad (\text{result for } N_c)$$

#### Evaluating $P_v$

$$P_v(T) = \int_{-\infty}^{E_v} g_v(E) e^{-\beta(E_v-E)} dE \quad (\text{from above})$$

$$= \frac{1}{2\pi^2} \left( \frac{2m_v^*}{\hbar^2} \right)^{3/2} \int_{-\infty}^{E_v} e^{-\beta(E_v-E)} \sqrt{|E_v - E|} dE$$

Let  $x \equiv \beta(E_v - E)$  (new integration variable)

$$P_v(T) = \frac{\sqrt{2}}{\pi^2} \left( \frac{m_v^* k_B T}{\hbar^2} \right)^{3/2} \int_0^{\infty} \sqrt{x} e^{-x} dx \quad (\text{in terms of } x)$$

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

$$P_v(T) = \frac{1}{4} \left( \frac{2m_v^* k_B T}{\pi \hbar^2} \right)^{3/2} \quad (\text{result for } P_v)$$

### Summary of Results: Charge Carrier Densities

$$n_e = \int_{E_c}^{\infty} g(E) f(E) dE \quad (\text{in general})$$

$$p_v = \int_{-\infty}^{E_v} f(E) g(E) dE \quad (\text{in general})$$

What follows assumes  $E_c - \mu \gg k_B T$  and  $\mu - E_v \gg k_B T$ !

$$n_c \approx e^{-\beta(E_c - \mu)} N_c(T)$$

$$p_v \approx e^{-\beta(\mu - E_v)} P_v(T)$$

$$N_c(T) = \frac{1}{4} \left( \frac{2m_c^* k_B T}{\pi \hbar^2} \right)^{3/2}$$

$$P_v(T) = \frac{1}{4} \left( \frac{2m_v^* k_B T}{\pi \hbar^2} \right)^{3/2}$$

$$n_c = \frac{1}{4} \left( \frac{2m_c^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{-\beta(E_c - \mu)} \quad (\text{approx. CB } e^- \text{ density})$$

$$p_v = \frac{1}{4} \left( \frac{2m_v^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{-\beta(\mu - E_v)} \quad (\text{approx. VB hole density})$$

### Intrinsic Semiconductors

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

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

$$\Rightarrow n_c = p_v \quad (\text{in intrinsic semiconductors})$$

Interpretation: The equality  $n_c = p_v$  expresses conservation of total electron number in intrinsic semiconductors.

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

#### Intrinsic Chare Carrier Density

The equality of  $n_c$  and  $p_v$  in intrinsic semiconductors motivates the definition of an *intrinsic carrier density*  $n_i$  given by...

$$n_c \equiv n_i \equiv p_v \quad (\text{intrinsic carrier density})$$

$$n_i^2 = n_c p_v = N_c P_v e^{-\beta(E_c - E_v)} \quad (\text{from above } n_c \text{ and } p_v)$$

$$= N_c P_v e^{-\beta E_g} \quad (\text{since } E_g = E_c - E_v)$$

$$\Rightarrow n_i = \sqrt{N_c P_v} e^{-\frac{\beta E_g}{2}}$$

#### Chemical Potential in Intrinsic Semiconductors

Goal: find an expression for the temperature dependence  $\mu(T)$  of an intrinsic semiconductor's chemical potential.

$$n_c = p_v \quad (\text{by definition of intrinsic SC})$$

$$n_c = p_v \Rightarrow N_c e^{-\beta(E_c - \mu)} = P_v e^{-\beta(\mu - E_v)}$$

$$e^{-\beta(E_c - \mu)} = \frac{P_v}{N_c} e^{-\beta(\mu - E_v)} \quad (\text{rearranged})$$

$$-\beta(E_c - \mu) = \ln \frac{P_v}{N_c} - \beta(\mu - E_v) \quad (\text{taking logarithm})$$

$$= \frac{3}{2} \ln \frac{m_v^*}{m_c^*} - \beta(\mu - E_v) \quad (\text{using } \frac{P_v}{N_c} = \left( \frac{m_v^*}{m_c^*} \right)^{3/2})$$

$$\mu(T) = \frac{1}{2}(E_c + E_v) + \frac{3}{4} k_B T \ln \frac{m_v^*}{m_c^*} \quad (\text{solving for } \mu)$$

Finally, use  $E_c = E_v + E_g \Rightarrow E_c + E_v = 2E_v + E_g$  to get...

$$\mu(T) = E_v + \frac{E_g}{2} + \frac{3}{4} k_B T \ln \frac{m_v^*}{m_c^*} \quad (\text{chem. pot. of an ISC})$$

#### Interpretation: Chemical Potential in Intrinsic SC

$$\mu(T) = E_v + \frac{E_g}{2} + \frac{3}{4} k_B T \ln \frac{m_v^*}{m_c^*} \quad (\text{for review})$$

$$E_F \equiv \mu(T)|_{T=0\text{K}} = E_v + \frac{E_g}{2} \quad (\text{Fermi energy in ISC})$$

Conclusion: an intrinsic semiconductor's Fermi energy lies exactly in the middle of the band gap

$$m_v^* \sim m_c^* \quad (\text{in typical materials and conditions})$$

$$\Rightarrow \ln \frac{m_v^*}{m_c^*} \lesssim 1 \quad (\text{since } m_v^* \sim m_c^*)$$

$$\Rightarrow \frac{3}{4} k_B T \ln \frac{m_v^*}{m_c^*} \lesssim k_B T \quad (\text{since } \ln \frac{m_v^*}{m_c^*} \lesssim 1)$$

Conclusion: the non-zero temperature deviation of  $\mu(T)|_{T>0}$  away from  $E_F = E_v + \frac{E_g}{2}$  is of the order  $k_B T$ .

Consequence: at temperatures for which  $k_B T \ll E_g$ , an intrinsic semiconductor obeys  $\mu(T) \approx E_g$ , and the non-degenerate semiconductor approximation  $E_c - \mu \ll k_B T$  and  $\mu - E_v \ll k_B T$  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

$$\begin{aligned} n_{\text{pure}} &\sim 5 \cdot 10^{22} \text{ cm}^{-3} && (\text{atom density in pure Si}) \\ n_i &\sim 10^{10} \text{ cm}^{-3} && (\text{intrinsic density in Si at } T \sim 300 \text{ K}) \\ N_d, N_a &\sim 10^{13} \text{ cm}^{-3} \text{ to } 10^{18} \text{ cm}^{-3} && (\text{typical dopant densities}) \end{aligned}$$

## Some General Considerations

Doped semiconductors are characterized by the relationships...

$$\begin{aligned} n_c - p_v &\neq 0 && (\text{in doped semiconductors}) \\ n_c p_v &= n_i^2 && (\text{in doped semiconductor}) \end{aligned}$$

$$\text{Let } \mu_i(T) \equiv E_v + \frac{E_g}{2} + \frac{3}{4} \ln \frac{m_v^*}{m_c^*} \quad (\text{in intrinsic SC})$$

$$\mu(T) \neq \mu_i(T) \quad (\text{in doped SC})$$

## 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...

- different effective masses  $m_c^*$  and  $m_v^*$  (via  $N_c$  and  $P_v$ )
- different energy levels  $E_v$  and  $E_c$
- different chemical potential  $\mu$

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  $\mu$ !

$$N_c^{(d)} \approx N_c^{(i)} \text{ and } P_v^{(d)} \approx P_v^{(i)} \quad (\text{due to low dopant densities})$$

$$n_c = N_c(T) e^{-\beta(E_c - \mu)}, \quad \mu \neq \mu_i \quad (\text{in doped SC})$$

$$p_v = P_v(T) e^{-\beta(\mu - E_v)}, \quad \mu \neq \mu_i \quad (\text{in doped SC})$$

## Extrinsic Carrier Densities I: CB Electrons

$$\text{Let } \Delta n \equiv n_c - p_v \quad (\text{difference in carrier densities})$$

$$n_c^2 - p_v n_c = n_c \Delta n \quad (\text{multiplying through by } n_c)$$

$$n_c^2 - n_c \Delta n - n_i^2 = 0 \quad (\text{using } n_i^2 = p_v n_c)$$

$$n_c = \frac{1}{2} \left[ \Delta n \pm \sqrt{\Delta n^2 + 4n_i^2} \right] \quad (\text{quadratic formula})$$

$$= \frac{1}{2} \left[ \Delta n + \sqrt{\Delta n^2 + 4n_i^2} \right] \quad (\text{use positive solution so } n_c > 0)$$

## Extrinsic Carrier Densities II: VB Holes

$$\Delta n = n_c - p_v \quad (\text{difference in carrier densities})$$

$$n_c p_v - p_v^2 = p_v \Delta n \quad (\text{multiplying through by } p_v)$$

$$p_v^2 + p_v \Delta n - n_i^2 = 0 \quad (\text{using } n_i^2 = n_c p_v)$$

$$p_v = \frac{1}{2} \left[ -\Delta n \pm \sqrt{\Delta n^2 + 4n_i^2} \right] \quad (\text{quadratic formula})$$

$$= \frac{1}{2} \left[ \sqrt{\Delta n^2 + 4n_i^2} - \Delta n \right] \quad (\text{use positive solution so } p_v > 0)$$

## Explicit Expression for Density Difference $\Delta n$

$$n_c = N_c e^{-\beta(E_c - \mu)} \quad (\text{in doped SC})$$

$$n_i = N_c e^{-\beta(E_c - \mu_i)} \quad (\text{in intrinsic SC})$$

$$\implies n_c = n_i e^{\beta(\mu - \mu_i)} \quad (\text{dividing } n_c \text{ by } n_i)$$

$$p_v = P_v e^{-\beta(\mu - E_v)} \quad (\text{in doped SC})$$

$$n_i = P_v e^{-\beta(\mu_i - E_v)} \quad (\text{in intrinsic SC})$$

$$\implies p_v = n_i e^{-\beta(\mu - \mu_i)} \quad (\text{dividing } p_v \text{ by } n_i)$$

$$\Delta n = n_c - p_v \quad (\text{by definition})$$

$$= n_i \left[ e^{\beta(\mu - \mu_i)} - e^{-\beta(\mu - \mu_i)} \right] \quad (\text{from just-derived } n_c \text{ and } p_v)$$

$$= 2n_i \sinh \left[ \beta(\mu - \mu_i) \right] \quad (\text{result: difference in densities})$$

# 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...

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e_0^2} \approx 0.05 \text{ nm} \quad (\text{Bohr radius; distance scale})$$

$$1 \text{ Ry} = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6 \text{ eV} \quad (\text{Rydberg energy; energy scale})$$

Group III		Group IV		Group V	
Al	3s <sup>2</sup> 3p <sup>1</sup>	Si	3s <sup>2</sup> 3p <sup>2</sup>	P	3s <sup>2</sup> 3p <sup>3</sup>
Ga	4s <sup>2</sup> 4p <sup>1</sup>	Ge	4s <sup>2</sup> 4p <sup>2</sup>	As	4s <sup>2</sup> 4p <sup>3</sup>

## Model for Levels of Donor Impurities

- Begin with a pure (intrinsic) semiconductor crystal made with volume density  $N_{\text{pure}}$  of group IV elements.
- Distribute group V donor impurities with donor density  $N_D \ll N_{\text{pure}}$  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 Ry  $\sim 10$  eV, but a donor electron embedded in a surrounding group IV lattice has greatly reduced binding energy because...

- The electric field of the positive nucleus binding the donor  $e^-$  is reduced by the SC's dielectric constant  $\epsilon \sim 15$ .
- 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  $e_0/\epsilon$ .

Replace  $m_e$  with  $m^*$  and  $\epsilon_0$  with  $\epsilon\epsilon_0$  in the expressions for  $a_0$  and 1 Ry to get...

$$r_0 \sim \frac{m_e}{m^*} \cdot a_0 \sim 100a_0 \quad (\text{donor } e^- \text{ distance scale})$$

$$E_b \sim \frac{m^*}{m_e} \frac{1}{\epsilon^2} \cdot \text{Ry} \sim 0.0005 \text{ Ry} \quad (\text{donor } e^- \text{ binding energy})$$

Conclusion: donor electrons have a far greater range and far lower binding energy than an  $e^-$  in an isolated hydrogen atom.

$$E_b \sim 0.0005 \text{ eV to } 0.01 \text{ eV} \quad (\text{typical donor } e^- \text{ binding energy})$$

$$k_B T|_{T \sim 300 \text{ K}} \sim 0.025 \text{ eV} \gg E_b \quad (k_B T \text{ at room temp.})$$

*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.

$$E_b \sim 0.0005 \text{ eV to } 0.01 \text{ eV} \quad (\text{typical acceptor hole } E_b)$$

$$k_B T|_{T \sim 300 \text{ K}} \sim 0.025 \text{ eV} \gg E_b \quad (k_B T \text{ at room temp.})$$

*Result: acceptor holes are easily freed from their acceptor ion cores as a result of room-temperature thermal fluctuations!*

## TODO: Energy Levels

Just introduce how the small binding energy for dopant charge carriers produces the new energy levels  $E_d$  just below  $E_c$  and  $E_a$  just above  $E_v$ , on a scale of  $E_g$ .

## 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.

$\mu$  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



$$Z_{gc} = \sum_j e^{-\beta(E_j - \mu N_j)} \quad (\text{GC partition function})$$

The average number  $\langle n \rangle$  of particles in the system is...

$$\begin{aligned} \langle n \rangle &= \frac{1}{Z_{gc}} \sum_j N_j e^{-\beta(E_j - \mu N_j)} \\ &= \frac{\sum_j N_j e^{-\beta(E_j - \mu N_j)}}{\sum_j e^{-\beta(E_j - \mu N_j)}} \end{aligned}$$

### Occupation Statistics of Donor Energy Levels

Consider a doped SC with donor density  $N_d \ll N_{\text{pure}}$

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*

$\Rightarrow n_d$  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;  $N = 1, E = E_d$
3. occupation by one spin down electron;  $N = 1, E = E_d$
4. occupation by two electrons with spin up and spin down;  $N = 2, E = 2E_d + E_{\text{repulsion}}$

Neglect double-electron occupation because large electrostatic repulsion  $E_{\text{repulsion}} \gg E_d$  makes occupation unlikely.

$$\begin{aligned} Z_{gc} &= \sum_j e^{-\beta(E_j - \mu N_j)} \\ &= 2 \cdot e^{-\beta(E_d - 1 \cdot \mu)} + e^{-\beta(0 - 0 \cdot \mu)} \\ &= 1 + e^{-\beta(E_d - \mu)} \end{aligned}$$

$$\begin{aligned} \sum_j N_j e^{-\beta(E_j - \mu N_j)} &= 2 \cdot (1 \cdot e^{-\beta(E_d - \mu)}) + 0 \cdot e^{-\beta \cdot 0} \\ &= 2e^{-\beta(E_d - \mu)} \end{aligned}$$

$$\begin{aligned} \langle n \rangle &= \frac{1}{Z_{gc}} \sum_j N_j e^{-\beta(E_j - \mu N_j)} \quad (\text{for a single donor site}) \\ &= \frac{2e^{-\beta(E_d - \mu)}}{1 + 2e^{-\beta(E_d - \mu)}} \quad (\text{using above } Z_{gc} \text{ and sum}) \\ &= \frac{1}{1 + \frac{1}{2}e^{\beta(E_d - \mu)}} \quad (\text{simplified}) \end{aligned}$$

$$\begin{aligned} n_d &= \langle n \rangle N_d \quad (\text{assuming donor } e^- \text{ are noninteracting}) \\ &= \frac{N_d}{1 + \frac{1}{2}e^{\beta(E_d - \mu)}} \quad (\text{donor } e^- \text{ occupation density}) \end{aligned}$$

### Occupation Statistics of Acceptor Energy Levels

Consider a doped SC with acceptor density  $N_a \ll N_{\text{pure}}$

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*

$\Rightarrow p_a$  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;  $N = 2, E = 2E_a$
2. occupation by one spin up electron/occupation by one hole;  $N = 1, E = E_a$
3. occupation by one spin down electron/occupation by one hole;  $N = 1, E = E_a$
4. occupation by zero electrons/occupation by two holes;  $N = 0, E = 0$ .

Neglect double-hole/zero-electron occupation because large electrostatic repulsion  $E_{\text{repulsion}} \gg E_a$  between two holes makes occupation unlikely.

$$Z_{gc} = \sum_j e^{-\beta(E_j - \mu N_j)} = e^{-\beta(2E_a - 2 \cdot \mu)} + 2e^{-\beta(E_a - 1 \cdot \mu)}$$

$$\sum_j N_j e^{-\beta(E_j - \mu N_j)} = 2 \cdot e^{-\beta(2E_a - 2\mu)} + 2 \cdot (1 \cdot e^{-\beta(E_a - \mu)})$$

$$\begin{aligned} \langle n \rangle &= \frac{1}{Z_{gc}} \sum_j N_j e^{-\beta(E_j - \mu N_j)} \quad (\text{for electrons in acceptor levels}) \\ &= \frac{2e^{-\beta(E_a - \mu)} + 2e^{-\beta(2E_a - 2\mu)}}{2e^{-\beta(E_a - \mu)} + e^{-2\beta(E_a - \mu)}} \\ &= \frac{2 + 2e^{-\beta(E_a - \mu)}}{2 + e^{-\beta(E_a - \mu)}} \quad (\text{dividing by } e^{-\beta(E_a - \mu)}) \end{aligned}$$

$$\begin{aligned} \langle p \rangle &= 2 - \langle n \rangle \quad (\text{electron-hole occupation relationship}) \\ &= 2 \cdot \frac{2 + e^{-\beta(E_a - \mu)}}{2 + e^{-\beta(E_a - \mu)}} - \frac{2 + 2e^{-\beta(E_a - \mu)}}{2 + e^{-\beta(E_a - \mu)}} \quad (\text{common denominator}) \end{aligned}$$

$$= \frac{1}{1 + \frac{1}{2}e^{\beta(\mu - E_a)}} \quad (\text{simplifying})$$

$$\begin{aligned} p_a &= \langle p \rangle N_a \quad (\text{assuming acc. holes are noninteracting}) \\ &= \frac{N_a}{1 + \frac{1}{2}e^{\beta(\mu - E_a)}} \quad (\text{acc. hole occupation density}) \end{aligned}$$

### Carrier Concentrations in Doped SCs

Goal: analyze how the intrinsic semiconductor relationship  $n_c = p_v$  generalizes to extrinsic semiconductor due to the addition of dopant energy levels.

#### Equilibrium Densities in a Doped SC if $N_d > N_a$

Consider an doped SC with dopant densities  $N_d > N_a$ .

Consider the SC's ground state configuration at  $T = 0$  K

At  $T = 0$  K,  $e^-$  will assume lowest possible energy configuration  $\Rightarrow N_a$  donor electrons drop into acceptor levels

At  $T = 0$  K if  $N_d > N_a$ ...

- Conduction band is fully empty
- Donor levels hold  $N_d - N_a$  electrons (i.e. as empty as the  $N_a < N_d$  available lower-energy acceptor levels allow)
- Acceptor levels are fully occupied with donor  $e^-$
- Valence band is fully occupied with valence  $e^-$

Summary: at  $T = 0$  K, acceptor/valence bands are full, and conduction/donor bands hold  $N_d - N_a$  electrons.

Idea: in thermal equilibrium at  $T > 0$  K, electrons will be redistributed among these levels, but the total electron number in the SC is conserved!

Consequence: at  $T > 0$  K, the density  $n_c + n_d$  of  $e^-$  in conduction and donor bands must exceed the  $T = 0$  K value of  $N_d - N_a$  by the number of  $e^-$  vacating the originally-full acceptor and valence bands, given by  $p_v + p_a$ .

$$\Rightarrow n_c + n_d = N_d - N_a + p_v + p_a \quad (\text{eq. densities in DSC})$$

#### Equilibrium Densities in a Doped SC if $N_a > N_d$

Consider an doped SC with dopant densities  $N_a > N_d$ .

Note: result is the same as derived above if  $N_d > N_a$ , i.e.

$$n_c + n_d = N_d - N_a + p_v + p_a$$

This section is given just as an exercise/alternative perspective.

Consider the SC's ground state configuration at  $T = 0$  K

At  $T = 0$  K,  $e^-$  will assume lowest possible energy configuration  $\Rightarrow$  all  $N_a$  donor electrons drop into acceptor levels

At  $T = 0$  K if  $N_a > N_d$ ...

- Conduction band is fully empty
- Donor levels are fully empty
- Acceptor levels hold  $N_d$  electrons (or  $N_a - N_d$  holes)
- Valence band is fully occupied with valence  $e^-$

Summary: at  $T = 0$  K, conduction/donor bands are fully empty, and acceptor/valence bands hold  $N_a - N_d$  holes

Idea: in thermal equilibrium at  $T > 0$  K, electrons (holes) will be redistributed among these levels, but the total electron (hole) number in the SC is conserved!

Consequence: at  $T > 0$  K, the density  $p_v + p_a$  of holes in valence and acceptor bands must exceed the  $T = 0$  K value of  $N_a - N_d$  by the number of electrons occupying the originally-empty donor and conduction bands, given by  $n_c + n_d$ .

$$\Rightarrow p_a + p_v = N_a - N_d + n_c + n_d \quad (\text{same as for } N_d > N_a!)$$

### Dopant Carrier Concentrations at Room Temperature

Consider a doped SC at room temp. where  $k_B T \sim 0.025$  eV  
 $E_b \sim 0.0005$  eV to  $0.01$  eV (typical dopant binding energy)  
( $E_c - E_d$ ), ( $E_a - E_v$ )  $\sim E_b \ll k_B T$

These relationships, together with the implicit non-degenerate SC approximation, permit the following assumptions...

Assume:  $E_d - \mu \gg k_B T$  (based on  $E_c - E_d \ll k_B T$ )

Assume:  $\mu - E_a \gg k_B T$  (based on  $E_a - E_v \ll k_B T$ )

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  $p_a \ll N_a$ ).

$$\begin{aligned}
n_c - p_v &\approx N_d - N_a & (\text{room temp. densities in DSC}) \\
n_c &\approx p_v + N_d & (\text{n-type SC at room temp.}) \\
p_v &\approx n_c + N_a & (\text{p-type SC at room temp.})
\end{aligned}$$

**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  $T = 0$  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  $\Rightarrow$  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  $E_d - \mu \gg k_B T$  and  $\mu - E_a \gg k_B T$

$$n_c - p_v \approx N_d - N_a \quad (\text{review: room temp. densities in DSC})$$

$$\Delta n \equiv n_c - p_v \quad (\text{from "Difference in Carrier Densities"})$$

$$\Delta n \approx N_d - N_a \quad (\text{at room temp.})$$

$$\Delta n \ll n_i \quad (\text{from assumption of light doping})$$

$$n_c = \frac{1}{2} \left[ \Delta n + \sqrt{\Delta n^2 + 4n_i^2} \right] \quad (\text{from "Diff. in Densities I"})$$

$$\approx n_i + \frac{1}{2}(N_d - N_a) + \mathcal{O}(\Delta n)^2 \quad (\text{for } \Delta n \ll n_i)$$

$$p_v = \frac{1}{2} \left[ \sqrt{\Delta n^2 + 4n_i^2} - \Delta n \right] \quad (\text{from "Diff. in Densities II"})$$

$$\approx n_i - \frac{1}{2}(N_d - N_a) + \mathcal{O}(\Delta n)^2 \quad (\text{for } \Delta n \ll n_i)$$

$$\begin{Bmatrix} n_c \\ p_v \end{Bmatrix} \approx n_i \pm \frac{1}{2}(N_d - N_a) \quad (\text{limit of light doping})$$

### Carrier Densities in Heavily-Doped Semiconductors

Consider a doped semiconductor in the room temperature limit where  $E_d - \mu \gg k_B T$  and  $\mu - E_a \gg k_B T$

$$n_c - p_v \approx N_d - N_a \quad (\text{review: room temp. densities in DSC})$$

$$\Delta n \equiv n_c - p_v$$

$$\Delta n \approx N_d - N_a \quad (\text{at room temp.})$$

$$\Delta n \gg n_i \quad (\text{from assumption of heavy doping})$$

$$n_c = \frac{1}{2} \left[ \Delta n + \sqrt{\Delta n^2 + 4n_i^2} \right] \quad (\text{from "Diff. in Densities I"})$$

$$\approx \begin{cases} \Delta n + \frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_d > N_a \\ -\frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_a > N_d \end{cases} \quad (\text{for } \Delta n \gg n_i)$$

$$p_v = \frac{1}{2} \left[ \sqrt{\Delta n^2 + 4n_i^2} - \Delta n \right] \quad (\text{from "Diff. in Densities II"})$$

$$\approx \begin{cases} \frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_d > N_a \\ -\Delta n - \frac{n_i^2}{\Delta n} + \mathcal{O}(n_i)^4 & N_a > N_d \end{cases} \quad (\text{for } \Delta n \gg n_i)$$

## 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  $\Delta x$  across the junction.

A necessary condition for semiclassical analysis is...

$$e\Delta\phi(\Delta x) \ll E_g \text{ for } \Delta x \sim a \quad (\text{for semiclassical analysis})$$

### Formation of the Depletion Region

Assume room temp. and  $E_d - \mu \ll k_B T$  and  $\mu - E_a \ll k_B T$

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!

$$d_{pn} \sim 10 \text{ nm to } 10^3 \text{ nm} \quad (\text{typical depletion region widths})$$

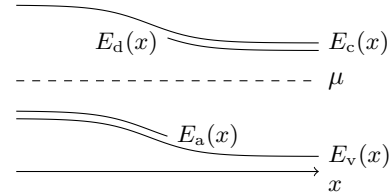
### Energy Levels Across Junction

Let  $\phi(x)$  denote electrostatic potential in p-n junction

$$E_c \rightarrow E_c - e_0\phi(x) \quad (\text{CB energy shifts due } \phi)$$

$$E_v \rightarrow E_v - e_0\phi(x) \quad (\text{VB energy shifts due } \phi)$$

Chemical potential  $\mu$  is constant across junction



$$n_c \rightarrow N_c(T)e^{-\beta(E_c - e_0\phi(x) - \mu)} \quad (\text{from shift in } E_c)$$

$$p_v \rightarrow P_v(T)e^{-\beta(\mu - E_v + e_0\phi(x))} \quad (\text{from shift in } E_v)$$

### Mathematical Analysis of the p-n Junction

This section implicitly assumes a room-temperature semiconductor obeying  $E_d - \mu \ll k_B T$  and  $\mu - E_a \ll k_B T$ !

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  $a \Rightarrow$  it is permissible to use *macroscopic* electrostatics equations to solve for  $\phi$ .

$$\nabla^2 \phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\epsilon\epsilon_0} \quad (\text{Poisson equation in 3D})$$

$$\frac{d^2 \phi}{dx^2} = -\frac{\rho(x)}{\epsilon\epsilon_0} \quad (\text{p-n junction properties vary only with } x)$$

### Boundary Conditions

Assume n-type conditions prevail for large positive  $x$

Assume p-type conditions prevail for large negative  $x$

$$\Rightarrow n_c(x \rightarrow \infty) = N_d \quad (\text{all donor electrons ionized})$$

$$\Rightarrow p_v(x \rightarrow -\infty) = N_a \quad (\text{all acceptor holes ionized})$$

Goal: relate boundary conditions to above expressions for carrier densities  $n_c$  and  $p_v$ .

### Conduction Band Electrons

$$n_c(x) = N_c e^{-\beta(E_c - e_0\phi(x) - \mu)} \quad (\text{review: CB } e^- \text{ density})$$

$$n_c(\infty) = N_d = N_c e^{-\beta(E_c - e_0\phi(\infty) - \mu)}$$

Divide  $n_c(x)$  by  $n_c(\infty)$  to get...

$$n_c(x) = N_d e^{-\beta e_0(\phi(\infty) - \phi(x))} = N_c e^{-\beta(E_c - e_0\phi(x) - \mu)} \quad (\text{alternate expression})$$

### Valence Band Holes

$$p_v(x) = P_v e^{-\beta(\mu - E_v + e_0\phi(x))} \quad (\text{review: VB hole density})$$

$$p_v(-\infty) = N_a = P_v e^{-\beta(\mu - E_v + \phi(-\infty))}$$

Divide  $p_v(x)$  by  $p_v(-\infty)$  to get...

$$p_v(x) = N_a e^{-\beta e_0(\phi(x) - \phi(-\infty))} = P_v e^{-\beta(\mu - E_v + e_0\phi(x))} \quad (\text{alternate expression})$$

### Relating Band Gap and Potential Drop

$$n_c(x) = N_d e^{-\beta e_0(\phi(\infty) - \phi(x))} = N_c e^{-\beta(E_c - e_0\phi(x) - \mu)}$$

$$p_v(x) = N_a e^{-\beta e_0(\phi(x) - \phi(-\infty))} = P_v e^{-\beta(\mu - E_v + e_0\phi(x))}$$

Multiply the two sides of above equations to get...

$$N_d N_a e^{-\beta e_0(\phi(\infty) - \phi(-\infty))} = N_c P_v e^{-\beta(E_c - E_v)}$$

$$\frac{N_d N_a}{N_c P_v} = e^{+\beta e_0(\phi(\infty) - \phi(-\infty))} \cdot e^{-\beta(E_c - E_v)} \quad (\text{rearranged})$$

$$\ln \frac{N_d N_a}{N_c P_v} = \beta e_0[\phi(\infty) - \phi(-\infty)] - \beta(E_c - E_v) \quad (\text{logarithmed})$$

$$e_0[\phi(\infty) - \phi(-\infty)] = E_c - E_v + k_B T \ln \frac{N_d N_a}{N_c P_v} \quad (\text{simplified})$$

$$e_0 \Delta \phi = E_g + k_B T \ln \frac{N_d N_a}{N_c P_v} \quad (\text{recognizing } E_g = E_c - E_v)$$

$\Delta \phi = \phi(\infty) - \phi(-\infty)$  is potential drop across p-n junction

$\phi(x) - \phi(-x) \approx \Delta \phi$  for  $|x| \sim 100 \text{ nm}$  (in practice)

### Simplified Expression for Charge Density

$$\frac{d^2 \phi}{dx^2} = -\frac{\rho(x)}{\epsilon \epsilon_0} \quad (\text{the Poisson equation})$$

Solving the Poisson equation requires an expression for  $\rho(x)$ !

$$\rho(x) = e_0 [N_d(x) - n_c(x) - (N_a(x) - p_v(x))] \quad (\text{generally, assuming ionized dopant levels})$$

$$N_d(x) = \begin{cases} 0 & x < 0 \\ N_d & x > 0 \end{cases} \quad (\text{review: assumed donor density})$$

$$N_a(x) = \begin{cases} N_a & x < 0 \\ 0 & x > 0 \end{cases} \quad (\text{review: assumed acceptor density})$$

$$n_c(x) = N_d e^{-\beta e_0(\phi(\infty) - \phi(x))} \quad (\text{in general; for review})$$

$$p_v(x) = N_a e^{-\beta e_0(\phi(x) - \phi(-\infty))} \quad (\text{in general; for review})$$

Complication: the above expression for  $\rho(x)$  is too complicated to analytically solve the Poisson equation.

Solution: use an approximate charge density given by...

$$\rho(x) \approx \begin{cases} 0 & x < -d_p \\ e_0 [N_d(x) - N_a(x)] & -d_p < x < d_n \\ 0 & x > d_n \end{cases} \quad (\text{derived below})$$

$$n_c p_v = n_i^2 \quad (\text{review: law of mass action})$$

### Outside Depletion Region

$$\phi(x > d_n) \sim \phi(\infty) \quad (\phi \text{ rapidly reaches asymptotic value})$$

$$\phi(x < -d_p) \sim \phi(-\infty) \quad (\phi \text{ rapidly reaches asymptotic value})$$

$$n_c(x > d_n) \sim N_d \quad (\text{since } \phi(x > d_n) \sim \phi(\infty) \text{ in n-type})$$

$$p_v(x < -d_p) \sim N_a \quad (\text{since } \phi(x < -d_p) \sim \phi(-\infty) \text{ in p-type})$$

$$p_v(x > d_n) \ll n_c(x > d_n) \quad (p_v \sim \frac{n_i^2}{N_d} \ll n_c \sim N_d \text{ in n-type})$$

$$n_c(x < -d_p) \ll p_v(x < -d_p) \quad (n_c \sim \frac{n_i^2}{N_a} \ll p_v \sim N_v \text{ in p-type})$$

$$\rho(x) = e_0 [N_d(x) - n_c(x) - (N_a(x) - p_v(x))] \quad (\text{generally})$$

$$\approx e_0 \begin{cases} [0 - (N_a - N_a)] & x < -d_p \\ [(N_d - N_d) - 0] & x > d_n \end{cases} = 0 \quad (\text{outside depletion region})$$

### Inside Depletion Region

$$e \Delta \phi \sim E_g \text{ across the depletion region } \Delta x = d_n + d_p$$

$$\text{Important: } E_g \gg k_B T \implies e \Delta \phi \gg k_B T$$

$$n_c(-d_p < x < d_n) \ll N_d(-d_p < x < d_n) \quad (\text{since } e \Delta \phi \gg k_B T)$$

$$p_v(-d_p < x < d_n) \ll N_a(-d_p < x < d_n) \quad (\text{since } e \Delta \phi \gg k_B T)$$

$$\rho(x) = e_0 [N_d(x) - n_c(x) - (N_a(x) - p_v(x))] \quad (\text{generally})$$

$$\approx e_0 [N_d(x) - N_a(x)] \quad (\text{inside depletion region})$$

### Result: Approximate Charge Density

Combine approximate expressions for  $\rho(x)$  inside and outside the depletion region to conclude that, except very near the DR boundaries  $x = -d_p$  or  $x = d_n$ ,  $\rho(x)$  obeys...

$$\rho(x) \approx \begin{cases} 0 & x < -d_p \\ e_0 [N_d(x) - N_a(x)] & -d_p < x < d_n \\ 0 & x > d_n \end{cases} \quad (\text{as quoted})$$

$$= \begin{cases} 0 & x < -d_p \\ -e_0 N_a & -d_p < x < 0 \\ e_0 N_d & 0 < x < d_n \\ 0 & x > d_n \end{cases} \quad (\text{written in full})$$

### Solving the Poisson Equation

Goal: solve the Poisson equation for  $\phi(x)$  using above  $\rho(x)$

$$\frac{d^2 \phi}{dx^2} = -\frac{\rho(x)}{\epsilon \epsilon_0} \quad (\text{Poisson equation})$$

$$\rho(x) = [N_d(x) - n_c(x) - (N_a(x) - p_v(x))] \quad (\text{generally})$$

$$= \begin{cases} 0 & x < -d_p \\ -e_0 N_a & -d_p < x < 0 \\ e_0 N_d & 0 < x < d_n \\ 0 & x > d_n \end{cases} \quad (\text{approximately})$$

$$\frac{d^2 \phi}{dx^2} = \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0} & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0} & 0 < x < d_n \\ 0 & x > d_n \end{cases} \quad (\text{Poisson equation})$$

### Solving Poisson Equation: First Integration

$$\frac{d\phi}{dx} = \begin{cases} \phi'(-\infty) & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0} x + A_p & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0} x + A_n & 0 < x < d_n \\ \phi'(\infty) & x > d_n \end{cases} \quad (\text{integrating } \phi''(x))$$

### Boundary Conditions

(i)  $\phi'$  is continuous at  $x = -d_p$  and at  $x = d_n$

(ii)  $\phi'$  is continuous at the p-n interface  $x = 0$

(iii)  $\phi'$  is constant for  $x < -d_p$  and  $x > d_n$

$$\phi'(-d_p^-) = 0 \equiv -\frac{e_0 N_a}{\epsilon \epsilon_0} d_p + A_p = \phi'(-d_p^+) \quad (\text{continuity at } -d_p)$$

$$\implies A_p = \frac{e_0 N_a}{\epsilon \epsilon_0} d_p$$

$$\phi'(d_n^-) = -\frac{e_0 N_d}{\epsilon \epsilon_0} d_n + A_n \equiv 0 = \phi'(d_n^+) \quad (\text{continuity at } d_n)$$

$$\implies A_n = \frac{e_0 N_d}{\epsilon \epsilon_0} d_n$$

$$\phi'(-\infty) = \phi'(\infty) = 0 \quad (\phi \text{ constant outside DR})$$

$$\implies \frac{d\phi}{dx} = \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0} (x + d_p) & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0} (x - d_n) & 0 < x < d_n \\ 0 & x > d_n \end{cases}$$

$$N_a d_p = N_d d_n \quad (\text{from continuity at } x = 0)$$

### Solving Poisson Equation: Second Integration

$$\phi(x) = \begin{cases} \phi(-\infty) & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0} \left( \frac{x^2}{2} + d_p x \right) + B_p & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0} \left( \frac{x^2}{2} - d_n x \right) + B_n & 0 < x < d_n \\ \phi(\infty) & x > d_n \end{cases} \quad (\text{int. } \phi')$$

### Boundary Conditions

(i)  $\phi$  is continuous at the p-n interface  $x = 0$

(ii)  $\phi(x)$  is continuous at  $x = -d_p$  and at  $x = d_n$

(iii)  $\phi(-\infty) \equiv 0 \implies \phi(\infty) = \Delta \phi$

$$B_p = B_n \equiv B \quad (\text{from first BC})$$

$$0 = -\frac{e_0 N_a}{2\epsilon \epsilon_0} d_p^2 + B \quad (\text{continuity at } -d_p)$$

$$\implies B = \frac{e_0 N_a}{2\epsilon \epsilon_0} d_p^2 \quad (\text{solving for } B)$$

$$\implies \phi(d_n) = \Delta \phi = \frac{e_0}{2\epsilon \epsilon_0} (N_d d_n^2 + N_a d_p^2) \quad (\text{cont. at } d_n)$$

$$\implies B = \frac{e_0 N_a}{2\epsilon \epsilon_0} d_p^2 = \Delta \phi - \frac{e_0 N_d}{2\epsilon \epsilon_0} d_n^2 \quad (\text{alt. expression for } B)$$

Substitute results into expression for  $\phi(x)$  to get...

$$\phi(x) = \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{\epsilon \epsilon_0} \left( \frac{x^2}{2} + d_p x \right) + \frac{e_0 N_a}{2\epsilon \epsilon_0} d_p^2 & -d_p < x < 0 \\ -\frac{e_0 N_d}{\epsilon \epsilon_0} \left( \frac{x^2}{2} - d_n x \right) + \Delta\phi - \frac{e_0 N_d}{2\epsilon \epsilon_0} d_n^2 & 0 < x < d_n \\ \Delta\phi & x > d_n \end{cases}$$

$$= \begin{cases} 0 & x < -d_p \\ \frac{e_0 N_a}{2\epsilon \epsilon_0} (x + d_p)^2 & -d_p < x < 0 \\ \Delta\phi - \frac{e_0 N_d}{2\epsilon \epsilon_0} (x - d_n)^2 & 0 < x < d_n \\ \Delta\phi & x > d_n \end{cases} \quad (\text{simplified})$$

### Depletion Region Width

Goal: determine depletion region width  $d_{pn}$  in terms of dopant densities  $N_a$ ,  $N_d$  and potential difference  $\Delta\phi$

$$N_a d_p = N_d d_n \quad (\text{from "Poisson Eq. 1st Int."})$$

$$\Delta\phi = \frac{e_0}{2\epsilon \epsilon_0} (N_d d_n^2 + N_a d_p^2) \quad (\text{from "Poisson Eq. 2nd Int."})$$

$$d_n^2 = \frac{2\epsilon \epsilon_0 \Delta\phi}{e_0 (N_a + N_d)} \frac{N_a}{N_d} \quad (\text{solved for } d_n)$$

$$d_p^2 = \frac{2\epsilon \epsilon_0 \Delta\phi}{e_0 (N_a + N_d)} \frac{N_d}{N_a} \quad (\text{solved for } d_p)$$

$d_{pn} = d_n + d_p$  and some algebra leads to...

$$d_{pn} = d_n + d_p = \sqrt{\frac{2\epsilon \epsilon_0 \Delta\phi}{e_0} \frac{N_a + N_d}{N_a N_d}} \quad (\text{DR width})$$

### 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

$$\Delta\phi = \Delta\phi_0 - V_b \quad (\text{with biasing})$$

$$\text{Let } C \equiv \sqrt{\frac{2\epsilon \epsilon_0}{e_0} \frac{N_a + N_d}{N_a N_d}} \quad (\text{for shorthand})$$

$$d_{pn}^{(0)} = \sqrt{C \Delta\phi_0} \quad (\text{from "Depletion Region Width"})$$

$$d_{pn} = \sqrt{C \Delta\phi} \quad (\text{generalized to include biasing})$$

$$= \sqrt{C (\Delta\phi_0 - V_b)}$$

$$d_{pn} = d_{pn}^{(0)} \sqrt{1 - \frac{V_b}{\Delta\phi_0}}$$

### 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

$$j_e = -e_0 J_e \quad (\text{electron current densities})$$

$$j_h = +e_0 J_h \quad (\text{hole current densities})$$

$$J_h = J_e = 0 \quad (\text{when } V_b = 0)$$

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*  $J_h^{\text{gen}}$ : minority-carrier holes flowing from n-type to p-type with the p-n electric field

2. *Recombination current*  $J_h^{\text{rec}}$ : 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.
- $J_h^{\text{gen}}$  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  $e^-$ .
- $J_h^{\text{rec}}$  falls with  $\Delta\phi$  as  $J_h^{\text{rec}} \propto e^{-e_0 \beta \Delta\phi_0}$

$$J_h(V_b) = J_h^{\text{rec}}(V_b) - J_h^{\text{gen}} \quad (\text{total hole current})$$

(assuming positive  $x$  from p-type to n-type)

### Relating Hole Gen. and Recombination Currents

$$J_h^{\text{rec}}(V_b) \propto e^{-\beta e_0 \Delta\phi} \quad (\text{review: hole gen. current})$$

$$= e^{-\beta e_0 (\Delta\phi_0 - V_b)} \quad (\text{using } \Delta\phi = \Delta\phi_0 - V_b)$$

$$\equiv J_0 e^{-\beta e_0 (\Delta\phi_0 - V_b)} \quad (\text{defining prop. constant } J_0)$$

$$J_h^{\text{rec}}(0) = J_0 e^{-\beta e_0 \Delta\phi_0} \quad (\text{when } V_b = 0)$$

Review:  $J_h = 0$  in thermal equilibrium when  $V_b = 0$

$$\Rightarrow J_h^{\text{gen}} = J_h^{\text{rec}}(V_b) \big|_{V_b=0} = J_0 e^{-\beta e_0 \Delta\phi_0}$$

Divide  $J_h^{\text{rec}}(V_b)$  by  $J_h^{\text{gen}} = J_0 e^{-\beta e_0 \Delta\phi_0}$  and rearrange to get...

$$J_h^{\text{rec}}(V_b) = J_h^{\text{gen}} e^{+\beta e_0 V_b} \quad (\text{hole recombination current})$$

$$J_h(V_b) = J_h^{\text{rec}}(V_b) - J_h^{\text{gen}} \quad (\text{total hole current})$$

$$= J_h^{\text{gen}} (e^{\beta e_0 V_b} - 1) \quad (\text{total hole current})$$

### Components of Electron Current

The current of  $e^-$  across the junction has two components...

1. *Generation current*  $J_e^{\text{gen}}$ : minority-carrier electrons flowing from p-type to n-type with the p-n electric field.
2. *Recombination current*  $J_e^{\text{rec}}$ : 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.
- $J_e^{\text{gen}}$  is independent of  $\Delta\phi$

#### Electron Recombination Current

- Mechanism:  $e^-$  in n-type excited to sufficient thermal energies overcome p-n potential barrier and reach p-type
- $J_e^{\text{rec}}$  falls with  $\Delta\phi$  as  $J_e^{\text{rec}} \propto e^{-e_0 \beta \Delta\phi}$

$$J_e(V_b) = J_e^{\text{gen}} - J_e^{\text{rec}}(V_b) \quad (\text{total electron current})$$

### Relating Electron Gen. and Recombination Currents

$$J_e^{\text{rec}}(V_b) \propto e^{-\beta e_0 \Delta\phi} \quad (\text{review: electron gen. current})$$

$$= e^{-\beta e_0 (\Delta\phi_0 - V_b)} \quad (\text{using } \Delta\phi = \Delta\phi_0 - V_b)$$

$$J_e^{\text{rec}}(V_b) \equiv J_0 e^{-\beta e_0 (\Delta\phi_0 - V_b)} \quad (\text{defining prop. constant})$$

$$J_e^{\text{rec}}(0) = J_0 e^{-\beta e_0 \Delta\phi_0} \quad (\text{when } V_b = 0)$$

Review:  $J_e = 0$  in thermal equilibrium when  $V_b = 0$

$$\Rightarrow J_e^{\text{gen}} = J_e^{\text{rec}}(V_b) \big|_{V_b=0} = J_0 e^{-\beta e_0 \Delta\phi_0}$$

Divide  $J_e^{\text{rec}}(V_b)$  by  $J_e^{\text{gen}} = J_0 e^{-\beta e_0 \Delta\phi_0}$  and rearrange to get...

$$J_e^{\text{rec}}(V_b) = J_e^{\text{gen}} e^{+\beta e_0 V_b} \quad (\text{electron recombination current})$$

$$J_e(V_b) = J_e^{\text{gen}} - J_e^{\text{rec}}(V_b) \quad (\text{total electron current})$$

$$= -J_e^{\text{gen}} (e^{\beta e_0 V_b} - 1) \quad (\text{total electron current})$$

### Total Electric Current Across Junction

$$j_h = +e_0 J_h$$

$$= e_0 J_h^{\text{gen}} (e^{\beta e_0 V_b} - 1)$$

$$j_e = -e_0 J_e$$

$$= e_0 J_e^{\text{gen}} (e^{\beta e_0 V_b} - 1)$$

$$j_{\text{tot}} = j_e + j_h \quad (\text{total electric current})$$

$$= e_0 (J_h^{\text{gen}} + J_e^{\text{gen}}) \cdot (e^{\beta e_0 V_b} - 1)$$

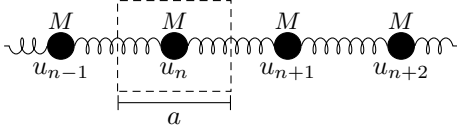
Motivation: in practice, the ions forming a crystal are not rigidly fixed, but may oscillate about their equilibrium positions.

## 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)

$\Rightarrow \langle R_n(t) \rangle = R_n^{(0)}$  (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)

$\Rightarrow e^{ik(N+1)a} \equiv e^{ika}$  (using  $u_{N+1} \equiv u_1$ )

$\Rightarrow e^{ikNa} = 1$  (simplifying)

$\Rightarrow kNa = 2\pi m$ ,  $m \in \mathbb{Z}$

$\Rightarrow k = \frac{2\pi}{Na} m$

Result: PBC require that  $k$  is discretized into  $N$  values

Convention: choose  $m$  such that...

$m \in \begin{cases} -\frac{N}{2}, \dots, \frac{N}{2} & N \text{ even} \\ -\frac{N-1}{2}, \dots, \frac{N-1}{2} & N \text{ odd} \end{cases}$

$\Rightarrow k \in \left(-\frac{\pi}{a}, \frac{\pi}{a}\right]$  ( $k$  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

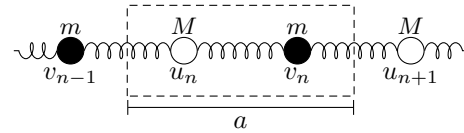
$\psi_k(n) = \sum_k A(k) u_0 e^{i(kna - \omega(k)t)}$  (wave packet ansatz)

$A(k)$  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  $d$  from 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  $K$

$U = \frac{K}{2} \sum_n [(u_n - v_n)^2 + (v_n - u_{n+1})^2]$  (lattice potential)

$F_{u_n} = -\frac{\partial U}{\partial u_n}$  (force on  $M$  ions)

$= -K(u_n - v_n) - K(u_n - v_{n-1})$

$= -K(2u_n - v_n - v_{n-1})$

$F_{v_n} = -\frac{\partial U}{\partial v_n}$  (force on  $m$  ions)

$= K(u_n - v_n) + K(u_{n+1} - v_n)$

$= -K(2v_n - u_n - u_{n+1})$

$M\ddot{u}_n = -K(2u_n - v_n - v_{n-1})$  (Newton's law for  $u_n$  ion)

$M\ddot{u}_n = -K(2v_n - u_n - u_{n+1})$  (Newton's law for  $v_n$  ion)

#### Solution and Dispersion Relation

$M\ddot{u}_n = -K(2u_n - v_n - v_{n-1})$  (Newton's law for  $u_n$  ion)

$m\ddot{v}_n = -K(2v_n - u_n - u_{n+1})$  (Newton's law for  $v_n$  ion)

$u_n(t) = u_0 e^{i(kna - \omega t)}$  (ansatz for solutions)

$v_n(t) = v_0 e^{i(kna - \omega t)}$  (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...

$$\begin{pmatrix} M\omega^2 - 2K & K(1 + e^{-ika}) \\ K(1 + e^{+ika}) & m\omega^2 - 2K \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0} \quad (\text{matrix form})$$

For a nontrivial solution for  $u_0$  and  $v_0$ , require...

$$\begin{aligned} 0 &\equiv \det \begin{pmatrix} M\omega^2 - 2K & K(1 + e^{-ika}) \\ K(1 + e^{+ika}) & m\omega^2 - 2K \end{pmatrix} \\ &= Mm\omega^2 - 2K(M + m)\omega^2 + 4K^2 - 2K^2(1 + \cos ka) \\ &= Mm\omega^2 - 2K(M + m)\omega^2 - 4K^2 \sin^2 \frac{ka}{2} \end{aligned}$$

Apply the quadratic formula to get the dispersion relation...

$$\begin{aligned} \omega_{\pm}^2 &= K \left( \frac{1}{m} + \frac{1}{M} \pm \sqrt{\left( \frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4}{mM} \sin^2 \frac{ka}{2}} \right) \\ &= K \frac{m+M}{mM} \left[ 1 \pm \sqrt{1 - \frac{4mM}{m+M} \sin^2 \frac{ka}{2}} \right] \end{aligned}$$

**Dispersion Relation: Acoustic Branch as  $k \rightarrow 0$**

First consider the acoustic branch  $\omega_-$  as  $k \rightarrow 0$

$$\begin{aligned} \omega_-^2 &= K \frac{m+M}{mM} \left[ 1 - \sqrt{1 - \frac{4mM}{m+M} \sin^2 \frac{ka}{2}} \right] \quad (\text{in general}) \\ &\rightarrow K \frac{m+M}{mM} \left[ 1 - \left( 1 - \frac{2mM}{(m+M)^2} \sin^2 \frac{ka}{2} \right) \right] \quad (\sqrt{1-x} \approx 1 - \frac{x}{2}) \\ &= \frac{2K}{m+M} \sin^2 \frac{ka}{2} \\ \omega_- &= +\sqrt{\frac{2K}{m+M}} \sin \frac{ka}{2} \quad (\text{take + sqrt. on physical grounds}) \\ &\approx \sqrt{\frac{K}{2(m+M)}} ka \quad (\text{using } \sin x = x + \mathcal{O}(x^3)) \end{aligned}$$

$$c_- = \frac{\omega_-}{k} = \sqrt{\frac{K}{2(m+M)}} a \quad (\text{constant phase velocity as } k \rightarrow 0)$$

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  $k \rightarrow 0$**

Next consider the optical branch  $\omega_+$  as  $k \rightarrow 0$

$$\begin{aligned} \omega_+^2 &= K \frac{m+M}{mM} \left[ 1 + \sqrt{1 - \frac{4mM}{m+M} \sin^2 \frac{ka}{2}} \right] \quad (\text{in general}) \\ &\rightarrow 2K \frac{m+M}{mM} \quad (\text{as } k \rightarrow 0) \\ \omega_+ &= \sqrt{2K \frac{m+M}{mM}} \end{aligned}$$

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  $k \rightarrow \frac{\pi}{a}$**

$$\begin{aligned} \omega_{\pm}^2 &= K \left[ \frac{m+M}{mM} \pm \sqrt{\left( \frac{1}{M} + \frac{1}{m} \right)^2 - \frac{4}{mM} \sin^2 \frac{ka}{2}} \right] \quad (\text{in general}) \\ &\rightarrow K \left[ \frac{m+M}{mM} \pm \sqrt{\left( \frac{1}{M} + \frac{1}{m} \right)^2 - \frac{4}{mM}} \right] \quad (\text{as } k \rightarrow \frac{\pi}{a}) \\ &= K \left[ \frac{m+M}{mM} \pm \sqrt{\left( \frac{1}{m} - \frac{1}{M} \right)^2} \right] \quad (\text{assuming } M > m) \\ &= \begin{cases} \frac{2K}{m} & \text{for } \omega_+ \\ \frac{2K}{M} & \text{for } \omega_- \end{cases} \end{aligned}$$

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

$$H = \sum_n \frac{p_n^2}{2M} + \frac{K}{2} (u_n - u_{n+1})^2 \quad (\text{lattice Hamiltonian})$$

Assume periodic boundary conditions of the form...

$$u_{N+1} = u_1 \quad (\text{assume periodic BC})$$

$$p_{N+1} = p_1 \quad (\text{assume periodic BC})$$

### Fourier Expansions of Position and Momentum

Plan: expand operators as Fourier series of the form...

$$u_n = \frac{1}{\sqrt{N}} \sum_k Q_k e^{ikna} \quad (\text{Fourier expansion of } u_n)$$

$$Q_k = \frac{1}{\sqrt{N}} \sum_n u_n e^{-ikna} \quad (\text{Fourier coefficients for } u_n)$$

$$p_n = \frac{1}{\sqrt{N}} \sum_k P_k e^{ikna} \quad (\text{Fourier expansion of } p_n)$$

$$P_k = \frac{1}{\sqrt{N}} \sum_n p_n e^{-ikna} \quad (\text{Fourier coefficients for } p_n)$$

$$k = \frac{2\pi}{Na} m \text{ where } m = 0, \pm 1, \dots, \pm \left( \frac{N}{2} - 1 \right), \frac{N}{2} \quad (\text{from BPC})$$

### Commutation Relations

$$[u_n, p_m] = i\hbar \delta_{nm} \quad (\text{review: canonical commutation relation})$$

Interpretation: operators associated with different ions commute

Goal: use  $[u_n, p_m] = i\hbar \delta_{nm}$  to find show  $[Q_k, P_{k'}] = i\hbar \delta_{kk'}$ .

$$[Q_k, P_{k'}] = \frac{1}{N} \sum_{n,n'} [u_n, p_{n'}] e^{i(k'n' - kn)a} \quad (\text{from above } u_n, p_n)$$

$$= \frac{i\hbar}{N} \sum_{n,n'} \delta_{nn'} e^{i(k'n' - kn)a} \quad (\text{using } [u_n, p_{n'}] = i\hbar \delta_{nn'})$$

$$= \frac{i\hbar}{N} \sum_n e^{i(k' - k)na} \quad (\text{using Kronecker delta } \delta_{nn'})$$

$$= \frac{i\hbar}{N} \sum_n e^{i \frac{2\pi}{N} (m' - m)n} \quad (\text{using } k = \frac{2\pi m}{Na})$$

$$= \frac{i\hbar}{N} \sum_{n=0}^{N-1} e^{i \frac{2\pi}{N} \ell n} \quad (\text{letting } \ell \equiv m' - m)$$

$$= \frac{i\hbar}{N} \frac{1 - e^{2\pi i \ell}}{1 - e^{i \frac{2\pi}{N} \ell}} \quad (\text{summing geometric series})$$

$$= \frac{i\hbar}{N} \begin{cases} N & \ell = 0 \\ 0 & \ell \in \mathbb{Z} \setminus \{0\} \end{cases} \quad (\text{L'Hôpital's rule for } 0/0)$$

$$= i\hbar \delta_{\ell,0} = i\hbar \delta_{m,m'} = i\hbar \delta_{k,k'}$$

$$[Q_k, P_{k'}] = i\hbar \delta_{k,k'} \quad (\text{result: commutator } [Q_k, P_{k'}])$$

### Hamiltonian in Terms of $P_k$ and $Q_k$

$$H = \sum_n \frac{p_n^2}{2M} + \frac{K}{2} (u_n - u_{n+1})^2 \quad (\text{in terms of } u_n \text{ and } p_n)$$

$$\frac{1}{N} \sum_n e^{i(k' - k)na} = \delta_{k,k'} \quad (\text{identity from above for reference})$$

$$H_{\text{kin}} = \sum_n \frac{p_n^2}{2M} = \frac{1}{2MN} \sum_{n,k,k'} P_k P_{k'} e^{i(k+k')na} \quad (\text{kinetic term})$$

$$= \frac{1}{2M} \sum_{k,k'} P_k P_{k'} \delta_{k,-k'} \quad (\text{see identity above})$$

$$= \frac{1}{2M} \sum_k P_k P_{-k} \quad (\text{using Kronecker delta } \delta_{k,-k'})$$

$$H_{\text{pot}} = \sum_n \frac{K}{2} (u_n - u_{n+1})^2 \quad (\text{potential term})$$

$$= \frac{K}{2N} \sum_{n,k,k'} Q_k Q_{k'} (e^{ikna} - e^{ik(n+1)a}) (e^{ik'n a} - e^{ik'(n+1)a})$$

$$= \frac{K}{2N} \sum_{n,k,k'} Q_k Q_{k'} (1 - e^{ika}) (1 - e^{ik'a}) e^{i(k+k')na}$$

$$= \frac{K}{2} \sum_{k,k'} Q_k Q_{k'} (1 - e^{ika}) (1 - e^{ik'a}) \delta_{k,-k'} \quad (\text{identify})$$

above)

$$= \frac{K}{2} \sum_k Q_k Q_{-k} (1 - e^{ika}) (1 - e^{-ika}) \quad (\text{using } \delta_{k,-k'})$$

$$= \frac{K}{2} \sum_k Q_k Q_{-k} (2 - 2 \cos ka) \quad (\text{exponential to sinusoid})$$

$$= K \sum_k Q_k Q_{-k} (1 - \cos ka) \quad (\text{simplifying})$$

$$\text{Let } K(1 - \cos ka) \equiv \frac{1}{2} M \omega_k^2 \quad (\text{defining frequency } \omega_k)$$

$$\omega_k = \sqrt{\frac{2K}{M} (1 - \cos ka)} \quad (\text{solving for } \omega_k)$$

$$= \sqrt{\frac{2K}{M} \cdot 2 \sin^2 \frac{ka}{2}} \quad (\text{using } 1 - \cos x = 2 \sin^2 \frac{x}{2})$$

$$= 2 \sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right| \quad (\text{simplifying})$$

$$H_{\text{pot}} = \frac{M}{2} \sum_k \omega_k^2 Q_k Q_{-k} \quad (\text{in terms of } \omega_k)$$

Combine kinetic and potential Hamiltonian terms to get...

$$H = H_{\text{kin}} + H_{\text{pot}} \quad (\text{Hamiltonian in terms of } P_k \text{ and } Q_k)$$

$$= \sum_k \left[ \frac{P_k P_{-k}}{2M} + K(1 - \cos ka) Q_k Q_{-k} \right]$$

$$= \sum_k \left( \frac{P_k P_{-k}}{2M} + \frac{M \omega_k^2}{2} Q_k Q_{-k} \right) \quad (\text{in terms of } \omega_k)$$

## Review: Miscellaneous Quantum Mechanics

The time evolution of an operator  $O$  in a system governed by the Hamiltonian  $H$  is...

$$i\hbar \frac{dO}{dt} = [Q, H] \quad (\text{time evolution of } O)$$

$$[A, BC] = B[A, C] + [A, B]C \quad (\text{commutator property})$$

## Review: Quantum Harmonic Oscillator

Consider a QHO of mass  $m$  and frequency  $\omega$ .

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left( x + \frac{i}{m\omega} p \right) \quad (\text{lowering operator})$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left( x - \frac{i}{m\omega} p \right) \quad (\text{raising operator})$$

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger + a) \quad (x \text{ in terms of } a \text{ and } a^\dagger)$$

$$p = i\sqrt{\frac{\hbar m\omega}{2}} (a^\dagger - a) \quad (p \text{ in terms of } a \text{ and } a^\dagger)$$

$$H_{\text{QHO}} = \frac{p^2}{2m} + \frac{m\omega^2}{2} x^2 \quad (\text{QHO's Hamiltonian})$$

$$= \hbar\omega \left( \frac{1}{2} + a^\dagger a \right) \quad (\text{in terms of } a \text{ and } a^\dagger)$$

$$[a, a^\dagger] = 1 \quad (\text{commutation relation})$$

Let  $|n\rangle$  where  $n = 0, 1, \dots$  denote  $n$ -th QHO eigenstate

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (\text{action of lowering operator})$$

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad (\text{action of raising operator})$$

$$a^\dagger a|n\rangle = n|n\rangle \quad (a^\dagger a \text{ is "counting" operator})$$

## 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 $Q_k$

$$i\hbar \dot{Q}_k = [Q_k, H] \quad (\text{by definition})$$

$$= [Q_k, H_{\text{kin}} + H_{\text{pot}}] \quad (\text{decomposing Hamiltonian})$$

$$= [Q_k, H_{\text{kin}}] \quad (Q_k \text{ commutes with all } Q_{k'} \text{ in } H_{\text{pot}})$$

$$= \left[ Q_k, \frac{1}{2M} \sum_{k'} P_{k'} P_{-k'} \right] \quad (\text{from expression for } H_{\text{kin}})$$

$$= \frac{1}{2M} \sum_{k'} P_{k'} [Q_k, P_{-k'}] + [Q_k, P_{k'}] P_{-k'} \quad (\text{comm. prop.})$$

$$= \frac{i\hbar}{2M} \sum_{k'} P_{k'} \delta_{k, -k'} + \delta_{k, k'} P_{-k'} \quad ([Q_k, P_{k'}] = i\hbar \delta_{kk'})$$

$$= 2 \frac{i\hbar}{2M} P_{-k} \quad (\text{using Kronecker deltas})$$

$$\Rightarrow \dot{Q}_k = \frac{1}{M} P_{-k} \quad (\text{result: time evolution of } Q_k)$$

### Second Time Evolution of $Q_k$

$$i\hbar \ddot{Q}_k = [\dot{Q}_k, H] \quad (\text{by definition})$$

$$= \frac{1}{M} [P_{-k}, H_{\text{pot}} + H_{\text{kin}}] \quad (\text{from above } \dot{Q}_k)$$

$$= \frac{1}{M} [P_{-k}, H_{\text{pot}}] \quad (P_{-k} \text{ commutes with all } P_k \text{ in } H_{\text{kin}})$$

$$= \frac{1}{M} [P_{-k}, \frac{M}{2} \sum_{k'} \omega_{k'}^2 Q_{k'} Q_{-k'}] \quad (\text{from above } H_{\text{pot}})$$

$$= \frac{1}{2} \sum_{k'} \omega_{k'}^2 (Q_{k'} [P_{-k}, Q_{-k'}] + [P_{-k}, Q_{k'}] Q_{-k})$$

$$= -\frac{i\hbar}{2} \sum_{k'} \omega_{k'}^2 (Q_{k'} \delta_{-k, -k'} + \delta_{-k, k'} Q_{-k'})$$

$$= -\frac{i\hbar}{2} \omega_k^2 (Q_k + Q_k) \quad (\text{using } [P_k, Q_{k'}] = -i\hbar \delta_{kk'})$$

$$\Rightarrow \ddot{Q}_k = -\omega_k^2 Q_k \quad (\text{result: time evolution of } \dot{Q}_k)$$

Rearrange to get...

$$\ddot{Q}_k + \omega_k^2 Q_k = 0 \quad (\text{equation for harmonic oscillator})$$

## Hamiltonian in Terms of Ladder Operators

$$H = \sum_k \left( \frac{P_k P_{-k}}{2M} + \frac{M\omega_k^2}{2} Q_k Q_{-k} \right) \quad (\text{review: lattice Ham.})$$

$$Q_k = \sqrt{\frac{\hbar}{2M\omega_k}} (a_k + a_{-k}^\dagger) \quad (\text{quoted})$$

$$P_k = i\sqrt{\frac{\hbar M\omega_k}{2}} (a_k^\dagger - a_{-k}) \quad (\text{quoted})$$

Justification: these definitions of  $Q_k$  and  $P_k$  preserve the commutation relation  $[Q_k, P_{k'}] = i\hbar \delta_{kk'}$  via  $[a, a^\dagger] = 1$ .

$$[Q_k, P_{k'}] = \frac{i\hbar}{2} [(a_k + a_{-k}^\dagger), (a_{k'}^\dagger - a_{-k'})] \quad (\text{proving com. rel.})$$

$$= \frac{i\hbar}{2} ([a_k, a_{k'}^\dagger] - [a_k, a_{-k'}] + [a_{-k}^\dagger, a_{k'}^\dagger] - [a_{-k}^\dagger, a_{-k'}])$$

$$= \frac{i\hbar}{2} ([a_k, a_{k'}^\dagger] - [a_{-k}^\dagger, a_{-k'}]) \quad ([a, a] = [a^\dagger, a^\dagger] = 0)$$

$$= i\hbar \delta_{kk'} \quad (\text{using } [a_k, a_{k'}^\dagger] = \delta_{kk'})$$

Substitute  $Q_k$  and  $P_k$  into lattice Hamiltonian to get...

$$H = \sum_k \left( \frac{P_k P_{-k}}{2M} + \frac{M\omega_k^2}{2} Q_k Q_{-k} \right) \quad (\text{review: lattice Ham.})$$

$$= -\frac{1}{2M} \frac{\hbar M}{2} \sum_k \omega_k (a_k^\dagger - a_{-k}) (a_{-k}^\dagger - a_k)$$

$$+ \frac{M}{2} \frac{\hbar}{2M} \sum_k \frac{\omega_k}{\omega_k} (a_k + a_{-k}^\dagger) (a_{-k} + a_k^\dagger)$$

$$= \frac{\hbar}{4} \sum_k \omega_k [(a_k + a_{-k}^\dagger) (a_{-k} + a_k^\dagger) - (a_k^\dagger - a_{-k}) (a_{-k}^\dagger - a_k)]$$

$$[a_k, a_{k'}] = 0 \Rightarrow a_k a_{k'} = a_{k'} a_k \quad \forall k, k' \quad (\text{for simplifying})$$

$$[a_k^\dagger, a_{k'}^\dagger] = 0 \Rightarrow a_k^\dagger a_{k'}^\dagger = a_{k'}^\dagger a_k^\dagger \quad \forall k, k' \quad (\text{for simplifying})$$

Multiply out Hamiltonian and simplify to get...

$$H = \frac{\hbar}{4} \sum_k \omega_k (a_k^\dagger a_k + a_{-k} a_{-k}^\dagger + a_{-k}^\dagger a_{-k} + a_k a_k^\dagger)$$

$$= \frac{\hbar}{4} \sum_k \omega_k (2a_k^\dagger a_k + 2a_k a_k^\dagger) \quad (\text{using } a_k = a_{-k}^\dagger)$$

$$= \sum_k \hbar \omega_k (a_k^\dagger a_k + \frac{1}{2}) \quad (\text{using } a_k a_k^\dagger = 1 + a_k^\dagger a_k)$$

$$= \sum_k H_{\text{QHO}}^{(k)} \quad (\text{result: sum of independent QHO})$$

## 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  $\{E_i\}$

$$Z_c = \sum_i e^{-\beta E_i} \quad (\text{canonical partition function})$$

$$u = \frac{1}{V Z_c} \sum_i E_i e^{-\beta E_i} \quad (\text{system's specific internal energy})$$

$$f = \frac{1}{V} \ln Z_c \quad (\text{defining the quantity } f)$$

$$= \frac{1}{V} \ln \left( \sum_i e^{-\beta E_i} \right) \quad (\text{substituting in } Z_c)$$

$$u = -\frac{\partial f}{\partial \beta} \quad (\text{internal energy in terms of } f)$$

$$c_V = \frac{\partial u}{\partial T} \quad (\text{specific heat capacity})$$

### Lattice's Internal Energy

Without derivation, a harmonic 3D lattice's total energy is...

$$E = \sum_{\mathbf{k}s} \left( n_{\mathbf{k}s} + \frac{1}{2} \right) \hbar \omega_s(\mathbf{k}) \quad (\text{lattice energy})$$

Heuristic justification: A harmonic lattice's Hamiltonian may be decomposed into a sum of uncoupled quantum harmonic oscillators  $\Rightarrow$  the total lattice energy should equal the sum of the energies of the individual QHO.

$$Z_c = \sum_i e^{\beta E_i} = \prod_{\mathbf{k}s} \left[ \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_s(\mathbf{k}) \left( n + \frac{1}{2} \right)} \right] \quad (\text{lattice's part.})$$

func.)

$$= \prod_{\mathbf{k}s} e^{-\beta \hbar \omega_s(\mathbf{k})/2} \left[ \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega_s(\mathbf{k})})^n \right]$$

$$= \prod_{\mathbf{k}s} \frac{e^{-\beta \hbar \omega_s(\mathbf{k})/2}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}} \quad (\text{summing the geometric series})$$

$$= \prod_{\mathbf{k}s} \frac{e^{-\beta \hbar \omega_s(\mathbf{k})/2}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}} \quad (\text{summing the geometric series})$$

$$f = \frac{1}{V} \ln Z_c = \frac{1}{V} \ln \prod_{\mathbf{k}s} \frac{e^{-\beta \hbar \omega_s(\mathbf{k})/2}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}} \quad (\text{lattice's value of } f)$$

$$= \frac{1}{V} \sum_{\mathbf{k}s} \ln \frac{e^{-\beta \hbar \omega_s(\mathbf{k})/2}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}} \quad (\text{using } \ln ab = \ln a + \ln b)$$

$$u = -\frac{\partial f}{\partial \beta} \quad (\text{in general})$$

$$= \frac{1}{V} \sum_{\mathbf{k}s} \left( \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} + \frac{1}{2} \right) \hbar \omega_s(\mathbf{k}) \quad (\text{lattice internal energy})$$

### Average Normal Mode Excitation Number

$$u = \frac{1}{V} \sum_{\mathbf{k}s} \left( \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} + \frac{1}{2} \right) \hbar \omega_s(\mathbf{k}) \quad (\text{review: internal energy})$$

$$E = \sum_{\mathbf{k}s} \left( n_{\mathbf{k}s} + \frac{1}{2} \right) \hbar \omega_s(\mathbf{k}) \quad (\text{review: total energy})$$

Recall  $u$  is (implicitly) the lattice's *average* internal energy

Compare expressions for  $E$  and  $u$  to conclude...

$$n_s(\mathbf{k}) = \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{mean excitation number})$$

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

$$u = \frac{1}{V} \sum_{\mathbf{k}s} \left( \frac{1}{e^{-\beta \hbar \omega_s(\mathbf{k})} - 1} + \frac{1}{2} \right) \hbar \omega_s(\mathbf{k}) \quad (\text{review: internal energy})$$

$$c_V = \frac{\partial u}{\partial T} = \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} \frac{\hbar \omega_s(\mathbf{k})}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1}$$

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  $T \rightarrow \infty$  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

$$c_V = \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} \frac{\hbar \omega_s(\mathbf{k})}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{for review})$$

Let  $x \equiv \beta \hbar \omega_s(\mathbf{k}) \implies x \ll 1$  for  $T \rightarrow \infty$

$$\frac{1}{e^x - 1} \approx \frac{1}{1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots - 1} = \frac{1}{x} \frac{1}{1 + \frac{x}{2} + \frac{x^2}{6}}$$

$$\approx \frac{1}{x} \left[ 1 - \left( \frac{x}{2} + \frac{x^2}{6} \right) + \left( \frac{x}{2} + \frac{x^2}{6} \right)^2 \right] \quad \left( \frac{1}{1+y} \approx 1 - y + y^2 \right)$$

$$= \frac{1}{x} \left[ 1 - \frac{x}{2} + \frac{x^2}{12} + \mathcal{O}(x^3) \right]$$

Use the expansion with  $c_V$  and  $x = \beta \hbar \omega_s(\mathbf{k})$  to get...

$$c_V \approx \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} \frac{\hbar \omega_s(\mathbf{k})}{\hbar \omega_s(\mathbf{k}) \beta} \left[ 1 - \frac{\hbar \omega_s(\mathbf{k}) \beta}{2} + \frac{1}{12} (\beta \hbar \omega_s(\mathbf{k}))^2 \right]$$

$$= \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} k_B T \left[ 1 - \frac{\hbar \omega_s(\mathbf{k})}{2k_B T} + \frac{(\hbar \omega_s(\mathbf{k}))^2}{12(k_B T)^2} \right] \quad (\text{in terms of } T)$$

$$= \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} \left[ k_B T - \frac{\hbar \omega_s(\mathbf{k})}{2} + \frac{(\hbar \omega_s(\mathbf{k}))^2}{12k_B T} \right] \quad (\text{simplifying})$$

$$= \frac{k_B}{V} \sum_{\mathbf{k}s} \left[ 1 - \frac{(\hbar \omega_s(\mathbf{k}))^2}{12(k_B T)^2} \right] \quad (\text{differentiating})$$

$$\rightarrow \frac{k_B}{V} \sum_{\mathbf{k}s} 1 \quad (\text{as } T \rightarrow \infty)$$

$$= \frac{k_B}{V} 3pN \quad (N \text{ values of } \mathbf{k} \text{ and } 3p \text{ branches})$$

Let  $n = \frac{3Np}{V}$  denote number density of ions in crystal to get...

$$c_V = 3nk_B \quad (\text{high-temperature limit})$$

Interpretation:  $c_V = 3nk_B$  is the law of Dulong and Petit

### Phonon Specific Heat: Low-Temperature Limit

$$c_V = \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} \frac{\hbar \omega_s(\mathbf{k})}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{for review})$$

$$\approx \frac{\partial}{\partial T} \sum_s \iiint_{\text{BZ}} \frac{\hbar \omega_s(\mathbf{k})}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \frac{d^3 \mathbf{k}}{(2\pi)^3} \quad (\text{approximating } \sum \text{ with } \int)$$

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...

$$\omega_s(\mathbf{k}) \approx c_s(\hat{\mathbf{k}})k \quad (\text{low-temperature approximation})$$

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  $\omega_s(\mathbf{k}) \approx c_s(\hat{\mathbf{k}})k$ .

$$c_V \approx \frac{1}{8\pi^3} \frac{\partial}{\partial T} \sum_s \iiint \frac{\hbar c_s(\hat{\mathbf{k}})k}{e^{\beta \hbar c_s(\hat{\mathbf{k}})k} - 1} d^3 \mathbf{k} \quad (\text{for low temperatures})$$

$$= \frac{1}{8\pi^3} \frac{\partial}{\partial T} \sum_s \iiint \frac{\hbar c_s(\hat{\mathbf{k}})k}{e^{\beta \hbar c_s(\hat{\mathbf{k}})k} - 1} k^2 dk d\Omega \quad (\text{to spherical coords.})$$

$$\text{Let } x \equiv \beta \hbar c_s(\hat{\mathbf{k}})k \quad (\text{new variable})$$

$$c_V = \frac{1}{8\pi^3} \frac{\partial}{\partial T} \sum_s \iiint \frac{d\Omega}{\beta^4 \hbar^4 c_s^3(\hat{\mathbf{k}})} \int_0^\infty \frac{x^3}{e^x - 1} dx \quad (\text{in terms of } x)$$

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \quad (\text{tabulated integral})$$

$$\text{Let } \frac{1}{c^3} \equiv \frac{1}{3} \sum_s \iint \frac{d\Omega}{4\pi c_s^3(\hat{\mathbf{k}})} \quad (\text{average speed over solid angle})$$

$$c_V = \frac{1}{8\pi^3} \frac{1}{\hbar^3} \frac{\partial}{\partial T} \frac{1}{\beta^4} \left( \frac{3 \cdot 4\pi}{c^3} \right) \cdot \frac{\pi^4}{15} \quad (\text{in terms of } c \text{ and integral})$$

$$= \frac{\pi^4}{10} \frac{1}{(\hbar c)^3} \frac{\partial}{\partial T} (k_B T)^4 \quad (\text{simplifying})$$

$$= \frac{2\pi^2}{5} k_B \left( \frac{k_B T}{\hbar c} \right)^3 \quad (\text{low-temperature limit})$$

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.

$$N_{\text{ion}} = pN \quad (\text{number of ions in the crystal})$$

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.

$$N_e = 2 \cdot \frac{V_F}{\Delta \mathbf{k}} = 2 \cdot \frac{4\pi k_F^3}{3} \frac{V}{8\pi^3} \quad (\text{factor 2 from } e^- \text{ spin})$$

$$= \frac{k_F^3}{6\pi^2} V \quad (\text{Fermi wave vector for } e^-)$$

$$\implies k_F^3 = 6\pi^2 \frac{N_e}{V} = 6\pi^2 n_e \quad (k_F \text{ in terms of } e^- \text{ density})$$

Analogy: the Debye wave vector is defined as the smallest radius in  $\mathbf{k}$  space enclosing exactly  $N_{\text{ion}}$  wave vectors.

$$N_{\text{ion}} = \frac{V_D}{\Delta \mathbf{k}} = \frac{4\pi k_D^3}{3} \frac{V}{8\pi^3} \quad (\text{phonons are spin-less; no 2 factor})$$

$$= \frac{k_D^3}{6\pi^2} V \quad (\text{Debye wave vector for phonons})$$

$$\implies k_D^3 = 3\pi^2 \frac{N_{\text{ion}}}{V} = 3\pi^2 n_{\text{ion}} \quad (k_D \text{ in terms of ion density})$$

### Debye Approximation: General Expression

$$\text{Let } \frac{1}{c^3} \equiv \frac{1}{3} \sum_s \iint \frac{d\Omega}{4\pi c_s^3(\hat{\mathbf{k}})} \quad (\text{average } c \text{ over acoustic branches})$$

$$c_V = \frac{1}{V} \frac{\partial}{\partial T} \sum_{\mathbf{k}s} \frac{\hbar \omega_s(\mathbf{k})}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{in general})$$

$$\approx \frac{\partial}{\partial T} \sum_s \iiint_{\text{BZ}} \frac{\hbar \omega_s(\mathbf{k})}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \frac{d^3 \mathbf{k}}{(2\pi)^3} \quad (\text{approximating } \sum \text{ with } \int)$$

$$\approx 3 \cdot \frac{1}{8\pi^3} \frac{\partial}{\partial T} \iiint_{\text{BZ}} \frac{\hbar ck}{e^{\beta \hbar \omega_k} - 1} d^3 \mathbf{k} \quad (\text{Debye: } \omega_s(\mathbf{k}) \rightarrow ck \forall 3 \text{ } s)$$

$$\approx \frac{3}{8\pi^3} \frac{\partial}{\partial T} \iiint \frac{\hbar ck}{e^{\beta \hbar \omega_k} - 1} d^3 \mathbf{k} \quad (\text{integrate over all } \mathbf{k})$$

$$= \frac{3}{8\pi^3} \frac{\partial}{\partial T} \iint d\Omega \int_0^{k_D} \frac{\hbar ck}{e^{\beta \hbar \omega_k} - 1} k^2 dk \quad (\text{to spherical coords.})$$

$$= \frac{3 \cdot 4\pi}{8\pi^3} \frac{\partial}{\partial T} \int_0^{k_D} \frac{\hbar ck^3}{e^{\beta \hbar \omega_k} - 1} dk \quad (\text{integrating over } d\Omega)$$

$$= \frac{3}{2\pi^2} \frac{(\hbar c)^2}{k_B T^2} \int_0^{k_D} \frac{k^4 e^{\beta \hbar ck}}{(e^{\beta \hbar \omega_k} - 1)^2} dk \quad (\text{differentiating})$$

$$\text{Let } x = \beta \hbar ck \quad (\text{new variable})$$

$$x_D \equiv x(k_D) = \frac{\hbar c}{k_B T} k_D \quad (\text{integration limit})$$

$$k_B \Theta_D = \hbar ck_D \quad (\text{definition of Debye temperature } \Theta_D)$$

$$c_V = \frac{3}{2\pi^2} \frac{k_B (\hbar c)^2 (k_B T)^5}{(k_B T)^2 (\hbar c)^5} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{in terms of } x)$$

$$= \frac{3k_B}{2\pi^2} \left( \frac{k_B T}{\hbar c} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{simplifying})$$

Multiply above/below by  $(k_B \Theta_D)^3$  and use  $k_D^3 = 6\pi^2 n_{\text{ion}}$  to get...

$$c_V = 9k_B n_{\text{ion}} \left( \frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{Debye: general result})$$

$$= \frac{3k_B}{2\pi^2} \left( \frac{k_B T}{\hbar c} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{alternate expression})$$

Problem: the expression is not analytically solvable

Resolution: observe limit cases of high and low temperature

### Debye Approximation: Low-Temperature Limit

$$x_D = \frac{\hbar c}{k_B T} k_D \quad (\text{for review})$$

$$\implies x_D \rightarrow \infty \text{ as } T \rightarrow 0$$

$$\int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \rightarrow \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15} \quad (\text{tabulated integral})$$

$$c_V = \frac{3k_B}{2\pi^2} \left( \frac{k_B T}{\hbar c} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{generally})$$

$$\begin{aligned} &\rightarrow \frac{3k_B}{2\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \frac{4\pi^4}{15} \quad (\text{as } T \rightarrow 0) \\ &= \frac{2\pi^2}{5} \left(\frac{k_B T}{\hbar c}\right)^3 k_B \quad (\text{Debye result: low-temp. limit}) \\ &= \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3 n_{\text{ion}} k_B \quad (\text{in terms of } \Theta_D) \end{aligned}$$

Note: agrees with earlier result in “**Low-Temp. Limit**”

### Debye Approximation: High-Temperature Limit

$$x_D = \frac{\hbar c}{k_B T} k_D \quad (\text{for review})$$

$$x_D \rightarrow 0 \text{ as } T \rightarrow \infty$$

$$x_D = \Theta_D / T \quad (\text{in general, for later use})$$

$$\int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \rightarrow 0 \quad (\text{as } T \rightarrow \infty)$$

Plan: expand integral for small  $x$  to get...

$$\begin{aligned} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} &\approx \int_0^{x_D} \frac{x^4 \cdot 1}{(1 + x - 1)^2} = \int_0^{x_D} x^2 dx \\ &= \frac{x_D^3}{3} = \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3 \quad (\text{using } x_D = \Theta_D / T) \end{aligned}$$

$$c_V = 9k_B n_{\text{ion}} \left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{in general})$$

$$\rightarrow 9k_B n_{\text{ion}} \left(\frac{T}{\Theta_D}\right)^3 \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3 \quad (\text{as } T \rightarrow \infty)$$

$$= 3n_{\text{ion}} k_B \quad (\text{Debye result: high-temp. limit})$$

Note: agrees with earlier result in “**High-Temp. 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.

$$c_V^{\text{ph}} = \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3 n_{\text{ion}} k_B \quad (\text{phonon specific heat; low } T)$$

Review: from “**Sommerfeld Expansion of Heat Capacity**”...

$$\begin{aligned} c_V^{\text{el}} &= \frac{\pi^2}{2} \frac{n_e}{E_F} k_B^2 T \quad (\text{electron specific heat}) \\ &= \frac{\pi^2}{2} \frac{T}{T_F} n_e k_B \quad (\text{in terms of Fermi temp. } T_F = E_F / k_B) \end{aligned}$$

Divide  $c_V^{\text{el}}$  by  $c_V^{\text{ph}}$  to get...

$$\begin{aligned} \frac{c_V^{\text{el}}}{c_V^{\text{ph}}} &= \frac{5}{24\pi^4} \frac{n_{\text{el}}}{n_{\text{ion}}} \frac{\Theta_D^3}{T^2 T_F} \\ &= \frac{5z}{24\pi^4} \frac{\Theta_D^3}{T^2 T_F} \quad (z = n_{\text{el}} / n_{\text{ion}} \text{ is number conduction } e^- \text{ per ion}) \end{aligned}$$

Let  $T_C$  denote crossover temperature where  $c_V^{\text{el}} / c_V^{\text{ph}} = 1$

$$T_C = \sqrt{\frac{5z}{24\pi^4} \frac{\Theta_D}{T_F}} \Theta_D \quad (\text{crossover btwn. dominance of } c_V^{\text{el}} / c_V^{\text{ph}})$$

$c_V^{\text{ph}}$  dominates above  $T_C$  and  $c_V^{\text{el}}$  below  $T_C$

For orientation:  $T_C \sim 5 \text{ K to } 10 \text{ K}$  (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  $c_V^{\text{ph}}$  from  $3n_{\text{ion}} k_B$  for  $T \gg \Theta_D$
- 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)

$$\begin{aligned} U(x) &= U_{\text{eq}} + cx^2 - gx^3 - fx^4 \quad (\text{quoted: ansatz for potential}) \\ &\equiv cx^2 - gx^3 - fx^4 \quad (\text{set eq. potential to zero}) \end{aligned}$$

$$|gx^3|, |fx^4| \ll |cx^2| \quad (\text{regime of validity})$$

#### Thermal Expansion

Plan: find expected value  $\langle x \rangle$  from eq. position for small  $x$

Note: calculation is highly approximate, results are qualitative.

$$Z = \int_0^\infty e^{-\beta E} dE \quad (\text{partition function})$$

$$= \int_{-\infty}^\infty e^{-\beta U(x)} dx \quad (\text{in terms of } x)$$

$$\langle x \rangle = \frac{1}{Z} \int_{-\infty}^\infty x e^{-\beta U(x)} dx \quad (\text{expected value of } x)$$

$$e^{-\beta U(x)} = e^{-\beta cx^2} e^{+\beta(gx^3 + fx^4)} \quad (\text{auxiliary approximation})$$

$$\approx e^{-\beta cx^2} (1 + \beta gx^3 + \beta fx^4) \quad (\text{for small } x)$$

$$\approx e^{-\beta cx^2} \quad (\text{neglecting } x^3 \text{ and } x^4)$$

$$\langle x \rangle = \frac{\int_{-\infty}^\infty x e^{-\beta U(x)} dx}{\int_{-\infty}^\infty e^{-\beta U(x)} dx} \quad (\text{review: exp. value of } x)$$

$$\approx \frac{\int_{-\infty}^\infty x (1 + \beta gx^3 + \beta fx^4) e^{-\beta cx^2} dx}{\int_{-\infty}^\infty e^{-\beta cx^2} dx} \quad (\text{with above approx.})$$

Shortcut: only even terms in numerator integrate to non-zero

$$\langle x \rangle = \frac{\int_{-\infty}^\infty \beta gx^4 e^{-\beta cx^2} dx}{\int_{-\infty}^\infty e^{-\beta cx^2} dx} \quad (\text{odd terms integrate to zero})$$

Let  $y^2 = \beta cx^2$  (new integration variable)

$$\langle x \rangle = \frac{g\sqrt{\beta c}}{\sqrt{\beta^3 c^5}} \frac{\int_{-\infty}^\infty y^4 e^{-y^2} dy}{\int_{-\infty}^\infty e^{-y^2} dy} \quad (\text{in terms of } y)$$

$$\int_{-\infty}^\infty e^{-y^2} dy = \sqrt{\pi} \quad (\text{tabulated integral})$$

$$\int_{-\infty}^\infty x^4 e^{-y^2} dy = \frac{3}{4} \sqrt{\pi} \quad (\text{tabulated integral})$$

$$\Rightarrow \langle x \rangle = \frac{3}{4} \frac{g}{\beta c^2} \quad (\text{result: expected deviation from eq.})$$

$$= \frac{3g}{4c^2} k_B T \propto T \quad (\text{in terms of } T)$$

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  $\tau$  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.

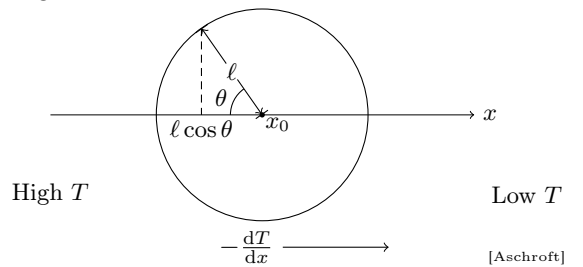
### Model and Geometry

Consider a lattice with a temperature gradient in the  $x$  direction.

$\vec{j} = j \hat{e}_x$  (heat current density, assuming 1D  $\nabla T$ )

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  $\ell$  from  $x_0$ .



### Finding Heat Current Density

Let  $u(x)$  denote energy density at position  $x$

Let  $c$  denote post-scattering phonon velocity

$$c_x = c \cos \theta \quad (\text{projection of } c \text{ onto } x \text{ axis})$$

$$j = \langle c_x \cdot u(x_0 - \ell \cos \theta) \rangle_\Omega \quad (\text{heat current density at } x_0)$$

$$= \frac{1}{4\pi} \iint c_x \cdot u(x_0 - \ell \cos \theta) d\Omega \quad (\text{avg. over solid angle})$$

$$= \frac{2\pi}{4\pi} \int_0^\pi (c \cos \theta) \cdot u(x_0 - \ell \cos \theta) \sin \theta d\theta \quad (2\pi \text{ from } \varphi)$$

Let  $y \equiv \cos \theta$  (new integration variable)

$$j = \frac{c}{2} \int_{-1}^1 y u(x_0 - \ell y) dy \quad (\text{in terms of } y)$$

$$= \frac{c}{2} \int_{-1}^1 y \left[ u(x_0) - \ell y \frac{\partial u}{\partial x} \Big|_{x_0} + \mathcal{O}(\ell y)^2 \right] dy \quad (\text{expanding } u(x))$$

$$\approx -\frac{c\ell}{3} \cdot \frac{\partial u}{\partial x} \Big|_{x_0} \quad (\text{evaluating integral to } \mathcal{O}(\ell y))$$

$$= -\frac{c\ell}{3} \frac{\partial u}{\partial T} \Big|_{x_0} \frac{\partial T}{\partial x} \Big|_{x_0} \quad (\text{chain rule})$$

$$= -\frac{c\ell}{3} c_V(x_0) \frac{\partial T}{\partial x} \quad (\text{recognizing } c_V = \frac{\partial u}{\partial T})$$

$$j(x) = -\frac{cl}{3}c_V(x)\frac{\partial T}{\partial x} \quad (\text{result: phonon heat current})$$

$$\text{Let } \kappa \equiv \frac{cl}{3}c_V = \frac{c^2\tau}{3}c_V \quad (\text{thermal conductivity})$$

$$j(x) = -\kappa\frac{\partial T}{\partial x} \quad (\text{in terms of thermal conductivity})$$

### Temperature Dependence of Thermal Conductivity

$$\kappa = \frac{cl}{3}c_V = \frac{c^2\tau}{3}c_V \quad (\text{review: thermal conductivity})$$

Contributions to  $\kappa(T)$  arise from...

- $c_V(T)$  (phonon heat capacity)
- $\tau(T)$  ( $T$ -dependence of scattering mean free time)
- $c(T) \approx \text{constant}$  (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.  $\sum_{\mathbf{k}s} n_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) = \sum_{\mathbf{k}s} n'_{\mathbf{k}s} \hbar \omega_s(\mathbf{k})$  (conservation of energy)
2.  $\sum_{\mathbf{k}s} \mathbf{k} n_{\mathbf{k}s} = \sum_{\mathbf{k}s} \mathbf{k} n'_{\mathbf{k}s} + \mathbf{K}$  (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 Brillouin zone!

### Phonon MFT: High-Temperature Limit

Consider behavior of  $n_s(\mathbf{k})$  for  $T \gg \Theta_D$ ...

$$\begin{aligned} n_s(\mathbf{k}) &= \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{in general (Bose-Einstein distribution)}) \\ &\approx \frac{1}{(1 + \beta \hbar \omega_s(\mathbf{k})) - 1} \quad (\text{expanding exp for } k_B T \gg \hbar \omega_s(\mathbf{k})) \\ &= \frac{k_B T}{\hbar \omega_s(\mathbf{k})} \quad (\text{high-temperature limit}) \end{aligned}$$

Assumption:  $\tau \sim 1/\sum n_s(\mathbf{k})$ . Interpretation: scattering increases (and  $\tau$  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  $T \gg \Theta_D$  MFT  $\tau$  scales as...

$$\begin{aligned} \tau &\sim \frac{1}{T} \quad (\text{theoretical phonon MFT for } T \gg \Theta_D) \\ \tau &\sim \frac{1}{T^x} \text{ with } x \in (1, 2) \quad (\text{typical measured behavior}) \end{aligned}$$

### Phonon MFT: Low-Temperature Limit I

$$\sum_{\mathbf{k}s} \mathbf{k} n_{\mathbf{k}s} = \sum_{\mathbf{k}s} \mathbf{k} n'_{\mathbf{k}s} + \mathbf{K} \quad (\text{review: conservation of } \mathbf{k})$$

Review:  $\mathbf{K}$  maps post-scattering wave vector  $\sum_{\mathbf{k}s} \mathbf{k} n'_{\mathbf{k}s}$  back into the first Brillouin zone (if necessary)

Idea: for  $T \ll \Theta_D$ , only phonons with frequency  $\omega_s(\mathbf{k}) \ll \omega_D$  and wave vector  $k \ll k_D$  occur appreciably.

Consequence: the  $\mathbf{k}$  of all phonons participating in scattering processes are  $\ll k_D \Rightarrow$  the total post-scattering wave vector  $\sum_{\mathbf{k}s} \mathbf{k} n'_{\mathbf{k}s}$  will lie *inside* the first Brillouin zone  $\Rightarrow \mathbf{K} = \mathbf{0}$ .

#### 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  $T \ll \Theta_D$  because  $\mathbf{K} = \mathbf{0}$

$$\sum_{\mathbf{k}s} \mathbf{k} n_{\mathbf{k}s} = \sum_{\mathbf{k}s} \mathbf{k} n'_{\mathbf{k}s} \quad (\text{normal processes})$$

$\Rightarrow$  normal processes conserve crystal momentum exactly

Plan: digress somewhat to discuss phonon heat current density, equilibrium, and normal processes. Return to MFT  $\tau$  at “Return to Equilibrium via Umklapp Processes”

### Phonon Heat Current Density

$$u = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) \quad (\text{lattice's phonon internal energy})$$

$$\mathbf{j}_{\text{ph}} = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) n_s(\mathbf{k}) \nabla_{\mathbf{k}} \omega_s(\mathbf{k}) \quad (\text{heat current density})$$

$$\approx \sum_s \iiint_{\text{BZ}} \hbar \omega_s(\mathbf{k}) n_s(\mathbf{k}) \nabla_{\mathbf{k}} \omega_s(\mathbf{k}) \frac{d^3 \mathbf{k}}{(2\pi)^3} \quad (\text{as an integral})$$

Interpretation:  $\mathbf{j}_{\text{ph}}$  is internal energy  $u$  times group velocity  $\mathbf{v}_g = \nabla_{\mathbf{k}} \omega_s(\mathbf{k})$  times phonon density  $n_s(\mathbf{k})$

Idea:  $\omega_s(\mathbf{k}) = \omega_s(-\mathbf{k}) \Rightarrow \nabla_{\mathbf{k}} \omega_s(\mathbf{k}) = -\nabla_{\mathbf{k}} \omega_s(-\mathbf{k})$

$\Rightarrow \omega_s(\mathbf{k})$  is even and  $\nabla_{\mathbf{k}} \omega_s(\mathbf{k})$  is odd  $\Rightarrow$  integrand in  $\mathbf{j}_{\text{ph}}$  is odd if  $n_s(\mathbf{k})$  is even, i.e. if  $n_s(\mathbf{k}) = n_s(-\mathbf{k})$

Conclusion:  $\mathbf{j}_{\text{ph}} \neq \mathbf{0}$  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:

$$n_s(\mathbf{k}) = \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{in thermal equilibrium})$$

$$\omega_s(\mathbf{k}) = \omega_s(-\mathbf{k}) \Rightarrow n_s(\mathbf{k}) = n_s(-\mathbf{k}) \quad (\text{in equilibrium})$$

Conclusion:  $n_s(\mathbf{k})$  is even in equilibrium, so  $\mathbf{j}_{\text{eq}} = \mathbf{0}$ .

Meanwhile:  $\mathbf{k}_{\text{tot}} = \mathbf{0}$  if  $n_s(\mathbf{k})$  is even, since  $n_s(\mathbf{k})$  even  $\Rightarrow \mathbf{k} \cdot n_s(\mathbf{k})$  is odd, which vanishes during  $\sum_{\mathbf{k} \in \text{BZ}}$

Conclusion:  $\mathbf{k}_{\text{tot}} = \mathbf{0}$  in equilibrium (when  $n_s(\mathbf{k})$  is even).

Meanwhile: consider normal processes only.

$$\sum_{\mathbf{k}s} \mathbf{k} n_s(\mathbf{k}) = \sum_{\mathbf{k}s} \mathbf{k} n'_s(\mathbf{k}) \quad (\text{for normal processes})$$

$$\Rightarrow \frac{d}{dt} \mathbf{k}_{\text{tot}} = \frac{d}{dt} \sum_{\mathbf{k}s} \mathbf{k} n_s(\mathbf{k}) = \mathbf{0} \quad (\mathbf{k}_{\text{tot}} \text{ conserved})$$

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  $\Rightarrow$  umklapp processes must be responsible for return to equilibrium.

Review: normal processes involve phonons with  $k \ll k_D$  and thus  $\omega_s(\mathbf{k}) \ll \omega_D$ . Consequence: umklapp processes involve phonons with  $\omega_s(\mathbf{k}) \gtrsim \omega_D$

$$n_s(\mathbf{k}) = \frac{1}{e^{\beta \hbar \omega_s(\mathbf{k})} - 1} \quad (\text{in general})$$

$$\sim \frac{1}{e^{\beta \hbar \omega_D} - 1} \quad (\text{for first occurring umklapp processes})$$

$$= \frac{1}{e^{\Theta_D/T} - 1} \quad (\text{in terms of } \Theta_D)$$

$$\approx e^{-\Theta_D/T} \quad (\text{in low-temp limit } T \ll \Theta_D)$$

Review:  $\tau \sim 1/\sum n_s(\mathbf{k})$ . Interpretation: scattering increases (and  $\tau$  decreases) with increasing phonon number  $n_{\mathbf{k}s}$ .

Since  $\tau \sim \frac{1}{n_s(\mathbf{k})}$  and  $n_s(\mathbf{k}) \sim e^{-\Theta_D/T}$ , for  $T \ll \Theta_D$  the phonon mean free time  $\tau$  scales as...

$$\tau \sim e^{\Theta_D/T} \quad (\text{theoretical phonon MFT for } T \ll \Theta_D)$$

$$\tau \sim e^{T_0/T} \text{ with } T_0 \sim \Theta_D \quad (\text{typical measured behavior})$$

### Phonon MFT: Low-Temperature Limit II

$$\tau \sim e^{\Theta_D/T} \quad (\text{review: phonon MFT for } T \ll \Theta_D)$$

In words: phonon-phonon scattering mean free time  $\tau$  increases exponentially for  $T \ll \Theta_D$ .

Naive conclusion: phonon thermal conductivity  $\kappa \propto T$  increases exponentially as  $T \rightarrow 0$  K

- In practice: as  $T \rightarrow 0$  K, phonon-phonon scattering  $\tau$  is dominated by  $\tau$  for phonon-impurity and phonon-surface scattering, and total  $\tau_{\text{tot}}$  remains finite as  $T \rightarrow 0$  K
- Additionally: phonon scattering MFP  $\ell \propto 1/\tau$  is bounded above by finite crystal size, so  $\tau$  reaches a constant max. value as  $T \rightarrow 0$  K.