

# Intro to Solid State Physics: Li Yang

## Contents

<b>Chapter 1: Crystal Structure</b>	<b>2</b>
<b>1 Lecture 1/25/24</b>	<b>3</b>
<b>2 Lecture 1/30/24</b>	<b>6</b>
<b>3 Lecture 2/1/24</b>	<b>8</b>
<b>4 Lecture 2/6/24</b>	<b>11</b>
<b>5 Lecture 2/8/24</b>	<b>14</b>
<b>6 Lecture 2/13/24</b>	<b>16</b>
<b>7 Lecture 2/15/24</b>	<b>19</b>
<b>8 Lecture 2/20/24</b>	<b>21</b>
<b>Chapter 2: Wave Diffraction and the Reciprocal Lattice</b>	<b>24</b>

## Chapter 1: Crystal Structure

**Ideal crystal is constructed by the infinite repetition of identical structural groups of atoms.** A group is called the basis. Detecting crystal structure started with x-rays due to the wavelength of the x-ray ( $\approx 1$  angstrom) being comparable to the interatomic spacing in a crystal.

**What is a *lattice*?** 2D Bravais Lattices [Wikipedia](#) The famous graphene has a hexagonal (honeycomb) structure like lattice, but it does not have the center atom from the true hexagonal lattice. The primitive of this lattice is made of up two atoms than can be translated to form the lattice. Thus graphene is like a diatomic crystal.

**3D Bravais Lattices** There are 14 Bravais lattices in 3D. In both 2D and 3D, the primitive cells that make up the lattice must fill the least amount of space and have no ‘holes’ or ‘extras’ left over. The 2 most common lattices now are the Primitive Hexagonal for its symmetry and the Body Centered Cubic (BCC) which is the lattice of Silicon, the most important material today.

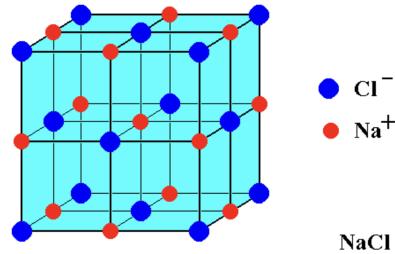


Figure 0.1: Sodium Chloride Structure (FCC)

**Example Structures** The lattice of Sodium Chloride is FCC as shown in Figure 0.1

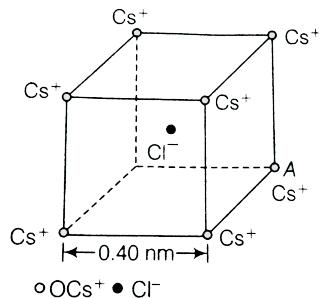


Figure 0.2: Cesium Chloride Structure (SC)

Figure 0.2 shows the lattice of Cesium Chloride which is SC.

# 1 Lecture 1/25/24

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## Chapter 3: cont'd

The momenta of the harmonic oscillators from last time are also in the ofmr 2 modes:

$$p_s = \frac{1}{\sqrt{2}}(p_1 + p_2) \quad p_a = \frac{1}{\sqrt{2}}(p_1 - p_2)$$

The matrix form

$$\begin{pmatrix} E_o & 0 \\ 0 & E_o \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \hbar\omega \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{vmatrix} E_o - \hbar\omega & \Delta \\ \Delta & E_o - \hbar\omega \end{vmatrix} = 0$$

solving for the eigenstates

$$\frac{1}{\sqrt{2}} \begin{pmatrix} a \\ b \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} a \\ -b \end{pmatrix}$$

The Hamiltonian of the single harmonic oscillator is

$$H_o = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

thus we can compare the frequencies of the harmonic oscillator and the Van der Waals interaction

$$\omega = \sqrt{\frac{c \pm \frac{2e^2}{R^3}}{m}}$$

and we know the *zero-point energy*  $1/2\hbar\omega$  or in this case

$$\frac{1}{2}\hbar\Delta\omega = \frac{1}{2}\hbar[\Delta\omega_s + \Delta\omega_a]$$

From the uncoupled sum and using Taylor expansion

$$\omega = \omega_o \left[ 1 \pm \frac{1}{2} \left( \frac{2e^2}{R^3 c} \right) \pm \frac{1}{8} \left( \frac{2e^2}{R^3 c} \right)^2 + \dots \right]$$

thus we ge the interaction energy

$$\Delta U = \frac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = \frac{\hbar\omega_o}{2} \left[ \frac{e^4}{c^2 R^6} \right] = -\frac{A}{R^6}$$

where the minus sign indicates an attractive force. We would expect the atoms to collapse, but this is not the case due to the Pauli exclusion principle (electrons cannot occupy the same state).

### Pauli exclusion principle

As the atoms get closer, there is an overlap of the wavefunctions. If the wavefunctions are symmetric, the spin states must be anti-symmetric. Therefore anti-symmetric wavefunctions have symmetric spin states. This repulsive force from the Pauli exclusion principle is typically found empirically  $\propto \frac{1}{R^{12}}$ . Therefore the total potential is

$$U(R) = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right]$$

AKA the Lennard-Jones potential. We could find the equilibrium distance by minimizing the potential  $\frac{dU}{dR} = 0$ . This is fine for inert gases that are spherical, but other molecules are depend on more than the scalar distance  $R$ . This decays faster than the scale of Coulombs Law  $\propto \frac{1}{R^2}$ . The total energy for a crystal is

$$E = \frac{1}{2}N(4\epsilon) \left[ \sum_j' \left( \frac{\sigma}{P_{ij}R} \right)^{12} - \sum_j' \left( \frac{\sigma}{P_{ij}R} \right)^6 \right]$$

where the prime indicates that the sum is over the nearest neighbors. The fcc lattice

$$\sum_j' \left( \frac{1}{P_{ij}} \right)^{12} = 12.13188; \quad \sum_j' \left( \frac{1}{P_{ij}} \right)^6 = 14.45392$$

for the 12 nearest neighbors. Solving for the minimum energy  $\frac{dU}{dR} = 0$  we get

$$R_o/\sigma = 1.09$$

### Ionic Crystal

The Coulomb interaction:

$$\pm \frac{q^2}{r_{ij}}$$

The short-term interaction

$$\lambda e^{-r_{ij}/\rho}$$

thus the potential is

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}$$

where at one site (one ion)

$$U_i = \sum_j' U_{ij}$$

and the total energy is

$$U = NU_i$$

For N molecules

$$U_{ij} = \begin{cases} \lambda e^{-r_{ij}/\rho} - \frac{q^2}{r_{ij}} & \text{nearest neighbor} \\ \pm \frac{q^2}{r_{ij}} & \text{otherwise} \end{cases}$$

and the total energy is

$$U_{tot} = N \left[ ze^{-R/\rho} - \alpha \frac{q^2}{R} \right] \quad \alpha = \sum_j' \frac{\pm}{p_{ij}}$$

where  $z$  is the number of nearest neighbors, and  $\alpha$  is the Madelung constant. From this we can find the lattice constant by using

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha \rho \frac{q^2}{z \lambda}$$

solving for  $R_o$  and putting into the total energy equation we get

$$U_{tot} = -\frac{N\alpha q^2}{R_o} \left(1 - \frac{\rho}{R_o}\right)$$

where we have a special term

$$-\frac{N\alpha q^2}{R_o}$$

known as the ‘Madelung Energy’.

## 2 Lecture 1/30/24

### Chapter 3: Bonds Bonds and Bonds

From last time:

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{q^2}{R} & \text{nearest neighbor} \\ \pm \frac{q^2}{p_{ij} R} & \text{otherwise} \end{cases}$$

where  $p_{ij}R = r_{ij}$  and the total energy (sum) is

$$U_{tot} = N \left[ z e^{-R/\rho} - \alpha \frac{q^2}{R} \right]$$

where  $z$  is the number of nearest neighbors,  $N$  is the total ions, and  $\alpha$  is the Madelung constant:

$$\alpha = \sum_j' \frac{\pm}{p_{ij}}$$

At the equilibrium separation

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha \rho \frac{q^2}{z \lambda}$$

$R_o$  is the equilibrium separation (position). Substituting this back into the total energy we get the empirical formula for the equilibrium energy (ground state):

$$U_{tot} = -\frac{N \alpha q^2}{R_o} \left( 1 - \frac{\rho}{R_o} \right)$$

where the first term outside the parenthesis is the Madelung energy

$$-\frac{N \alpha q^2}{R_o}$$

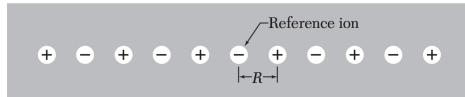


Figure 2.1: Line of ions with alternating charges

**The Evaluation of Madelung Constant** Letting  $R$  denote the distance between the ions, we can write the Madelung constant for the 1D line of ions with alternating charges as.

$$\begin{aligned} \frac{\alpha}{R} &= 2 \left[ \frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} + \dots \right] \\ &= \frac{2}{R} \left[ 1 - \frac{1}{2} + \dots \right] \\ \alpha &= 2 \ln 2 \end{aligned}$$

Remember these numbers

- Bohr radius  $a_o = 0.529 \text{ \AA}$
- fine structure constant  $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$

For the covalent bond, we have to use QM because the electron distribution is homogenous like a sea of electrons. Sometimes we think of this as a homogenous electron gas. This is a very difficult problem to solve. So we move on to the Hydrogen bond. This is a very weak bond typically at the scale of meV—room temperature is around 25 meV. So the bonds can break easily.

## Chatper 4: Phonons (lattice vibration)

First starting with the 1D case: evenly spaced atoms we can take the minimum energy energy at the atom and take the limit as it approaches zero or

$$\frac{\partial U}{\partial x} = 0$$

the first term is  $V \propto x^2$  so we can approximate the potential as

$$U = \frac{1}{2}U''x^2 = \frac{1}{2}cx^2$$

where  $c$  is the spring constant. So we can imagine that the atoms  $(u_{s-1}, u_s, u_{s+1})$  are connected by springs. For 2 coupled springs in series we end up with 2 eigenmodes. But we look at each pair of atoms and sum up the forces. Using newton's second law we get the force of the  $s$  atom

$$F_s = c(u_{s+1} - u_s) + c(u_{s-1} - u_s) = c[u_{s+1} + u_{s-1} - 2u_s]$$

or as a differential equation

$$\begin{aligned} M \frac{d^2 u_s}{dt^2} &= c[u_{s+1} + u_{s-1} - 2u_s] \\ u &= u(\gamma)e^{-i\omega t} \\ \implies -M\omega^2 u_s &= c[u_{s+1} + u_{s-1} - 2u_s] \end{aligned}$$

this momentum of the crystal is not conserved but the Hamiltonian can still be written as

$$H(\gamma)H(\gamma + T)$$

where we discretize the translational symmetry, so we can write the periodic part of the atom as

$$u_s^k = ue^{-ik\gamma} \quad u(\gamma)=u(\gamma+T)$$

where  $k = 2\pi/L$  is the wavevector. So we can write the  $u_{s-1}$  and  $u_{s+1}$  as a translation of  $u_s$ :

$$\begin{aligned} u_{s-1} &= ue^{-i(s-1)ka} \\ u_{s+1} &= ue^{i(s+1)ka} \\ u_s &= ue^{-iska} \end{aligned}$$

where  $a$  is the lattice spacing. subbing this back in:

$$\begin{aligned} -M\omega^2 &= c[e^{-ika} + e^{ika} - 2] \\ \omega^2 &= 2\frac{c}{M}(1 - \cos(ka)) \end{aligned}$$

using the trig identity for half angles we get

$$\omega^2 = \frac{4c}{M} \sin^2\left(\frac{ka}{2}\right) \quad \text{or} \quad \omega = 2\sqrt{\frac{c}{M}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

where  $\omega = ck$  is the dispersion relation where we have boundaries at  $\pm\pi/a$  and max  $2\sqrt{c/m}$ . The group velocity is

$$v_g = \frac{\partial \omega}{\partial k}$$

for  $k \rightarrow 0$  we get the group velocity

$$v_g = a\sqrt{\frac{c}{M}}$$

we also get from the graph of  $\omega$  is that the slope at the boundaries are zero.

### 3 Lecture 2/1/24

#### Chapter 4: cont'd

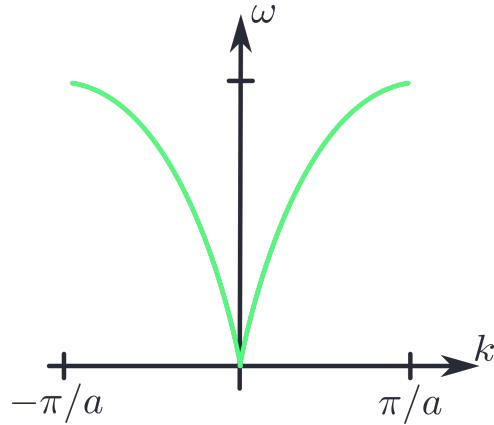


Figure 3.1: Graph of  $\omega$  vs  $k$

Graphing  $\omega$  vs  $k$  we get the graph in Figure 3.1. The slope at the boundaries is zero, and the maximum is  $2\sqrt{c/M}$ . But as  $k \rightarrow 0$  we know that  $\omega = 0$  and the energy is also zero. We can imagine the atoms are moving in phase (oscillating in the same direction) and amplitude. For  $\omega = 2\sqrt{c/M}$  we have the atoms moving out of phase (moving in opposite of their neighbors with equal amplitude). At this point  $k = \pi/a$  the potential is

$$e^{i\pi/a \cdot a} \rightarrow e^{i\pi}$$

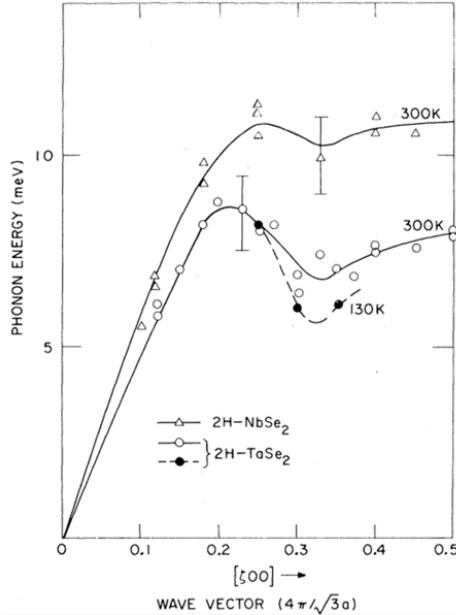


Figure 3.2: Graph of  $\omega$  vs  $k$  for different material and temperature

Figure 3.2 shows the graph of  $\omega$  vs  $k$  for neutron scattering observed in different materials and temperatures. We can see that the lower temperature has a low energy mode.

**Aside:** For phonons in low temperature, we see a double well potential, but for high temperatures, we see negative potential as shown in Figure 3.2.

**Two atom per unit cell** (primitive basis) For the 1D case again:

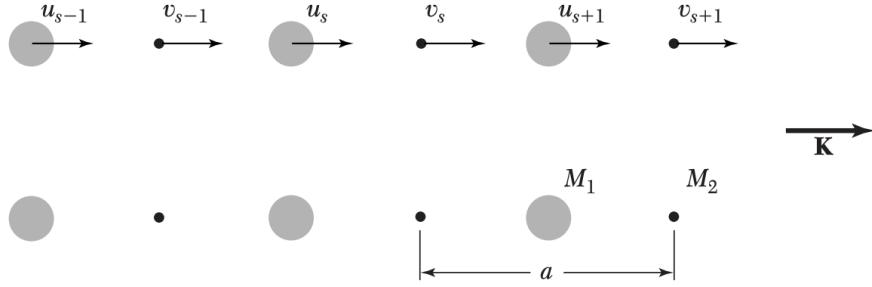


Figure 3.3: Two atom per unit cell

Using newton's second law

$$\begin{aligned} M_1 \ddot{u}_s &= c[v_s + v_{s-1} - 2u_s] \\ M_2 \ddot{v}_s &= c[u_s + u_{s+1} - 2v_s] \end{aligned}$$

and the periodic nature of the lattice

$$\begin{aligned} u_s &= ue^{isk a} e^{-i\omega t} \\ v_s &= ve^{isk a} e^{-i\omega t} \end{aligned}$$

from substitution we get

$$\begin{aligned} -M_1 \omega^2 u &= cv[1 + ve^{-ika}] - 2u \\ -M_2 \omega^2 v &= cu[1 + ue^{ika}] - 2v \end{aligned}$$

or in matrix form

$$-\omega^2 \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = c \begin{pmatrix} -2c & c[1 + e^{-ika}] \\ c[1 + e^{ika}] & -2c \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} \quad (3.1)$$

to find the eigenvalues we solve the determinant of the matrix. We can only do this if the matrix is real (hermitian: complex conjugate is the same as the original). Solving for zero

$$A = \begin{vmatrix} -\omega^2 M_1 + 2c^2 & -c^2(1 + e^{-ika}) \\ -c^2(1 + e^{ika}) & -\omega^2 M_2 + 2c^2 \end{vmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = 0$$

and the determinant of  $A$  is

$$\begin{aligned} \omega^4 M_1 M_2 - 2c^2 \omega^2 (M_1 + M_2) + 4c^4 + c^2(1 + e^{-ika})(1 + e^{ika}) &= 0 \\ \omega^4 (M_1 M_2 - 2c^2(M_1 + M_2) + 4c^4 - c^4[2 + 2 \cos(ka)]) &= 0 \end{aligned}$$

for  $k = 0$  we get

$$M_1 M_2 w^4 - 2c[M_1 + M_2]\omega^2 = 0$$

we get the solutions

$$\begin{aligned} \omega_o &= 0 \\ \omega_1 &= \sqrt{\frac{2c(M_1 + M_2)}{M_1 M_2}} \end{aligned}$$

for  $k = \pi/a$  we get

$$\omega^4 M_1 M_2 - 2c\omega^2 (M_1 + M_2) + 4c^4 = 0$$

Physically, the  $k = 0$  mode there are two solutions, one where all basis move in the same direction, and the other where each atom moves in the opposing direction. For  $k = \pi/a$  we have a solution where the basis pair move in the opposite direction of its neighbors. For this special case, we know that the Brillouin zone is half the size of the original zone, so the zone folds in half.

**Phonon modes** For the  $k = 0$ , in the  $\omega_o = 0$  case we know that  $\lambda \rightarrow \infty$  and it is called an acoustic phonon, but for  $\omega_1$  this is an optical phonon. This is in the order of meV around the room temperature. For energy of the phonon,

$$E = \hbar\omega = pc \quad \text{and} \quad p = \hbar k$$

Raman scattering is related to the scattering of light from the optical phonon. The wavelength of incoming and outgoing light shift by the energy of the phonon.

**3D Case:**  $N$  atoms per unit cell. We have  $3N$  branches of phonons. 3 acoustic and  $3N - 3$  optical phonon.

## 4 Lecture 2/6/24

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### Chapter 4: cont'd

**Raman Scattering & Infrared** (THz)  $\sim 100$  meV. For the 3D case, we have 3 acoustic modes and  $3N - 3$  optical modes. For the acoustic mode.

$$k \rightarrow 0, \quad \omega \rightarrow 0$$

and for the optical modes

$$k \rightarrow 0, \quad \omega \rightarrow \infty$$

### Chapter 5: Phonon properties

The heat capacity is in general

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v$$

The proportionality of heat capacity in different materials

- Metal:  $C_v \propto I + QT^3$
- Insulator:  $C_v \propto T^3$

The Energy of an  $N$  particle system is  $E = Nk_B T$ . and the heat capacity is

$$C_v = \frac{\partial E}{\partial T} = \omega k_B$$

The total energy is

$$U_{tot} = \sum k, p \hbar \omega_{k,p} \langle n_{k,p} \rangle$$

where  $\langle n_{k,p} \rangle$  is the Bose-Einstein distribution

$$\langle n_\omega \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

where there is no chemical potential. At low temperatures the constant goes to

$$\exp\left(\frac{\hbar\omega}{k_B T}\right)$$

or a boltzmann distribution.

$$U_{tot} \sum_{k,p} \frac{\hbar \omega_{k,p}}{\exp\left(\frac{\hbar \omega_{k,p}}{k_B T}\right) - 1}$$

or into an integral

$$\int dk f(\omega) \rightarrow \int d\omega f(\omega) \frac{1}{\frac{d\omega}{dk}}$$

We can compute this numerically from the phonon dispersion relation. For the Heat capacity of a solid, this  $T^3$  term is in the order of 3 meV. We only need to take the acoustic modes into account for finding  $\frac{d\omega}{dk}$  which approximately a constant  $C$ , so

$$\int_0^a d\omega \frac{\hbar \omega^2}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1}$$

where we can simplify using the substitution

$$x = \frac{\hbar\omega}{k_B T}$$

to change the integral from  $k$  space to  $\omega$  space and the integral becomes

$$T^2 \int_0^\infty dx \frac{x}{\exp(x) - 1}$$

where the  $T^2$  term comes from substituting for  $\omega$  twice. So the total energy is

$$U_{tot} = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

where  $D_p(\omega)$  is the density of states. Using the substitution for  $x$  we get

$$U_{tot} = \sum_p \int \omega d\omega D_p(\omega) \frac{x}{e^x - 1}$$

and the heat capacity is

$$C_v = \frac{\partial U_{tot}}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2}$$

The density of states (DOS) is given by

$$D(\omega) = \frac{dN}{d\omega}$$

where  $N$  is the number of states. For a 3D phonon gas, the total allowed states is

$$N = \frac{\frac{4}{3}\pi k^3}{\left(\frac{2\pi}{L}\right)^3}$$

Which is equivalent to the volume of a sphere for each unit volume. So the DOS is

$$D(\omega) = \frac{dN}{d\omega} = \frac{dN}{dk} \frac{dk}{d\omega} = \frac{V}{2\pi^2} \frac{k^2}{1}$$

and the heat capacity is

$$C_v \propto k_B \sum_p \int d\omega \frac{k^2 V}{2\pi^2} \frac{1}{\frac{d\omega}{dk}} \frac{x^2 e^x}{(e^x - 1)^2}$$

and since  $\omega = vk$  and  $\frac{d\omega}{dk} = v$  we get

$$C_v \propto \sum_p \int_0^{\omega_D} d\omega \frac{V}{1} \frac{\omega^2}{v^3} \frac{x^2 e^x}{(e^x - 1)^2}$$

so we get the number of states

$$N = \int_0^{\omega_D} d\omega D(\omega)$$

where

$$\omega_D^2 = \frac{6\pi^2 N}{V}$$

the total energy is

$$U_{tot} = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2T^2v^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

and substituting for  $x$  we get

$$\propto T^4 \int_0^{x_D} dx x^2 \frac{x}{e^x - 1}$$

where we have four  $x$  terms that are substituted thus the  $T^4$  term. We get Debye's law for the heat capacity

$$U_{tot} \propto T^4 f(x_D) \quad C_v = \frac{\partial U}{\partial T} \propto T^3$$

for low temperature  $T \rightarrow 0$ ,  $x_D \rightarrow \infty$  so the  $f(x_D) \rightarrow 1$  which will give us Debye's law. Some constants:  $\omega_D$  is the Debye frequency and the Debye temperature is

$$\theta_D = \frac{\hbar\omega_D}{k_B}$$

### Einstein Model

$$D(\omega) = N\delta(\omega - \omega_0)$$

so we get a simple expression for the total energy

$$U_{tot} \propto \frac{\hbar\omega_o}{\exp\left(\frac{\hbar\omega_o}{k_B T}\right) - 1}$$

and the heat capacity is

$$C_v = \frac{\partial U}{\partial T} \Big|_{T \rightarrow 0} \propto \frac{1}{T} \frac{\exp\left(\frac{\hbar\omega_o}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_o}{k_B T}\right) - 1\right)^2} \rightarrow T \exp\left(\frac{\hbar\omega_o}{k_B T}\right)$$

For the einstein model we get a wrong number because we assumed the density of states is a delta functions ,but it reality it is a constant.

## 5 Lecture 2/8/24

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### Chapter 6: Free Electron Fermi Gas

Read [Slater Determinant](#): We typically use an approximation of the wavefunction for  $N$  fermions as

$$E\psi_N = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_N$$

found using the [Hartree-Fock method](#) where we use the Slater determinant to find the energy of the system. For a system of  $N$  fermions we have a periodic potential and we can approximate this  $N$  fermions to one mean-field. Also related: [Dyson Equation](#). When we treat the group of particles as one *mean-field* we call them *quasiparticles*. The quasiparticle must obey the charge conservation e.g. a bare electron drags a positive cloud which also drags nearby electrons as a quasi electron and the total charge of the dragged cloud is still -1. We desire small mass quasi particles for semiconductors due to a faster acceleration. For the free-electron case we assume that the electrons do not interact with each other thus, we can quantize the single electron states.

**Energy** The quantized energies are related to the quantized standing waves of the particle in a box. The Hamiltonian is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n = E_n \psi_n$$

which has a sinusoidal solution of the wavefunction

$$\psi_n = A \sin\left(\frac{2\pi}{\lambda_n} x\right)$$

and the boundary condition determines the wavelength

$$n\lambda_n = 2L$$

and thus the energy of a state is

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{n\pi}{L} \right)^2$$

**Fermi (level) energy** is pretty much the highest occupied state (energy). For the 1D case the wave number can only be satisfied at the states for the standing waves:

$$k_0 = 0, \quad k_2 = \pm \frac{2\pi}{L}, \quad k_4 = \pm \frac{4\pi}{L}, \quad \dots$$

the fermi level at  $N$  is

$$k = \frac{N\pi}{2L} \rightarrow \epsilon_f = \frac{\hbar^2}{2m} \left( \frac{N\pi}{2L} \right)^2$$

For the 3D case, we have a cube with a small box of volume  $(\frac{2\pi}{L})^3$  and for the large number  $10^{23}$  we get a rough estimate of a spherical shell. The fermi energy is

$$\frac{\frac{4}{3}\pi k_f^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{N}{2}$$

where the  $N/2$  comes from the degeneracy of the spin states. This is equivalent to the ratio of the volume of the sphere to the volume element. The fermi momentum is

$$k_f = \left( \frac{3}{8} \sqrt{(2\pi)^3 L^3} \frac{1}{\pi} \right)^{1/3}$$

or

$$K_f = \left( \frac{3\pi^2 N}{V} \right)^{1/3}$$

and the fermi energy is

$$\epsilon_f = \frac{\hbar^2}{2m} k_f^2 = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}$$

and the electron velocity is

$$v_f = \frac{\hbar k_f}{m} = \frac{\hbar}{m} \left( \frac{3\pi^2 N}{V} \right)^{1/3}$$

much like the phonon example, we can find the density of states for the free electron gas:

$$D(\epsilon) = \frac{dN}{d\epsilon}$$

we can solve the fermi energy equation as a function of energy

$$N = \left( \frac{2\epsilon m}{\hbar^2} \right)^{3/2} \frac{V}{3\pi^2}$$

we also have a relation between  $N$  and  $k_f$  so we can write the volume in  $k$  space:

$$V_k = \frac{4}{3}\pi k^3$$

and since the energy is quantized as

$$E = \frac{\hbar^2 k^2}{2m} \rightarrow k = \frac{\sqrt{2mE}}{\hbar}$$

thus

$$V_k = \frac{4}{3}\pi \frac{(2mE)^{3/2}}{\hbar^3}$$

and since the number of states is

$$\begin{aligned} N &= \frac{V_k}{\left(\frac{2\pi}{L}\right)^3} \cdot 2 \\ &= \frac{V}{3\pi^2} \left( \frac{2mE}{\hbar^2} \right)^{3/2} \end{aligned}$$

thus the density of states is

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

so the DOS is proportional to  $\sqrt{E}$ . Also it is proportional to the mass!

## 6 Lecture 2/13/24

### Chapter 6: Cont'd

**Fermi Energy** We have a 3D free electron gas with a DOS of

$$D(\epsilon) = \square \epsilon^{1/2}$$

For the 2D case we have

$$D(\epsilon) = \text{const}$$

which will look like a Heaviside step function. For the 1D case we have

$$D(\epsilon) = \frac{1}{\sqrt{\epsilon}}$$

where we have the energy dispersion relation

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

for graphene (2D material) what does the DOS look like? We would expect it to look like step function, but the electron dispersion relation is linear:  $\epsilon = ck$  so the DOS is a linear function.

**weird li yang writing:**

$$C_v \propto \alpha T^3 + \beta T$$

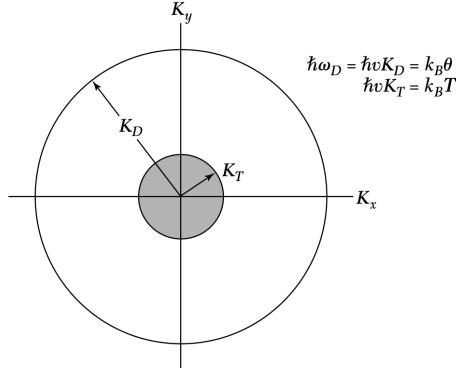


Figure 6.1: Fermi sphere

**Fermi sphere** at roughly 30 K the classical thermal energy is roughly  $k_B T \sim 3$  meV. As the temperature goes up, there is a smearing of the shell at the edges of the fermi sphere. So there are more electrons that can be excited to higher energy states thus  $N \propto k_B T$ . The fermi energy is then roughly  $N k_B T \approx T^2 \propto U$ . And the heat capacity is

$$C_v \propto \frac{\partial U}{\partial T} \propto T$$

**Fermi-Dirac distribution** We have 3 parameters that describe the distribution

$$f(T, \epsilon, \mu) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1}$$

For  $T \rightarrow 0$ , if  $\epsilon > \mu$  then  $f \rightarrow 0$  and if  $\epsilon < \mu$  then  $f \rightarrow 1$ . at very small temperatures, we have a step function. As  $T$  increases, the energy states are more smoothed out.

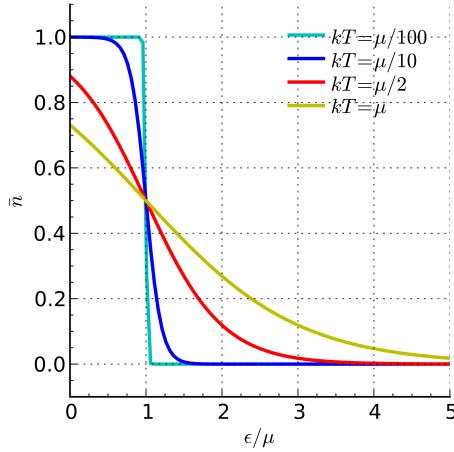


Figure 6.2: Fermi-Dirac distribution

### Energy change

$$\Delta U = U(T) - U(0)$$

for  $U(0)$  we have

$$U(0) = \int_0^{\epsilon_f} d\epsilon D(\epsilon) \epsilon$$

where we are taking the density of energy and multiplying by the energy at each state and summing them up from 0 to  $\epsilon_f$ . For  $U(T)$  we have

$$\begin{aligned} U(T) &= \int_0^{\infty} d\epsilon D(\epsilon) \epsilon f(\epsilon) \\ &= \left( \int_0^{\epsilon_f} + \int_{\epsilon_f}^{\infty} \right) d\epsilon D(\epsilon) \epsilon f(\epsilon) \end{aligned}$$

where we can split this integral into two parts. So we get the change in energy

$$\Delta U = \int_{\epsilon_f}^{\infty} [\epsilon - \epsilon_f] f(\epsilon) D(\epsilon) d\epsilon + \int_0^{\epsilon_f} [\epsilon_f - \epsilon] [1 - f(\epsilon)] D(\epsilon) d\epsilon$$

where the first term  $I$  is the part to the right of the chemical potential and the second term  $II$  is the part to the left of the chemical potential. We can then find the chemical potential in reference to the zero energy state.:

$$\begin{aligned} C_v = \frac{d(\Delta U)}{dT} &= \int_{\epsilon_f}^{\infty} d\epsilon (\epsilon - \epsilon_f) \frac{\partial f}{\partial T} D(\epsilon) + \int_0^{\epsilon_f} d\epsilon (\epsilon_f - \epsilon) \left( -\frac{\partial f}{\partial T} \right) D(\epsilon) \\ &= \int_0^{\infty} d\epsilon (\epsilon - \epsilon_f) \frac{\partial f}{\partial T} D(\epsilon) \end{aligned}$$

where we first redefine  $\tau = k_B T$ , and

$$f(\epsilon, \tau, \mu) = \frac{1}{\exp\left(\frac{\epsilon-\mu}{\tau}\right) + 1}$$

so

$$\frac{\partial f}{\partial T} = k_B \frac{\partial f}{\partial \tau} = \frac{\epsilon - \epsilon_f}{\tau^2} \frac{\exp\left(\frac{\epsilon-\mu}{\tau}\right)}{\left(\exp\left(\frac{\epsilon-\mu}{\tau}\right) + 1\right)^2}$$

as  $\mu/\epsilon_f$ . We can define another variable

$$x = \frac{\epsilon - \mu}{\tau}$$

So

$$C_v = k_B^2 T D(\epsilon_f) \int_{-\epsilon_f/\tau}^{\infty} dx x^2 \frac{\exp(x)}{(\exp(x) + 1)^2}$$

and at  $T \rightarrow 0$  we get reduce this to

$$C_v = k_B^2 T D(\epsilon_f) \int_{-\infty}^{\infty} dx x^2 \frac{\exp(x)}{(\exp(x) + 1)^2}$$

and the analytical solution gives us

$$\frac{\pi^2}{3}$$

e.g. for the free electron gas with a DOS

$$D(\epsilon_f) = \frac{3N}{2k_B T_f}$$

the heat capacity is

$$C_v = \frac{1}{2}\pi^2 N k_B \frac{T}{T_f}$$

**Electrical Conductivity** for an electron the force is

$$\begin{aligned} \mathbf{F} &= -e\mathbf{E} = m \frac{d\mathbf{v}}{dt} = \hbar \frac{d\mathbf{k}}{dt} \\ m \frac{d\mathbf{v}}{dt} &= -eE \quad \Delta U = -\frac{eE}{m} \Delta t \end{aligned}$$

From the Drude model, we have a mean free path that explains the motion of the electrons. This  $\Delta t$  is related to teh scattering (where high  $\tau$  means less scattering). And from the Drude model we can define the current density:

$$\mathbf{j} = ne\mathbf{v} = n \frac{e^2 \tau \mathbf{E}}{m}$$

with conductance

$$\sigma = \frac{ne^2 \tau}{m}$$

the overall collision time is

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots$$

So applying an electric field will shift the center of the fermi sphere since the electric field will apply a force on the electrons.

## 7 Lecture 2/15/24

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### Chapter 6: Cont'd

From the conductance eq, we usually see that well conductive materials have a lighter effective mass.

**Hall Effect:** Consider a 2D material with a longitudinal electric field  $E_x$  and a orthogonal magnetic field  $\mathbf{H} = B_z$ . There will be a resulting voltage drop(electric field) in the transverse direction  $E_y$ : We first define the longitudinal conductance

$$\rho(H) = \frac{E_x}{J_x}$$

and the Hall coefficient is

$$R_H = \frac{E_y}{J_x H}$$

from the Lorentz force we have

$$\frac{d\mathbf{p}}{dt} = q(\mathbf{E} + \frac{\mathbf{p}}{m} \times \mathbf{H}) - \frac{\mathbf{p}}{\tau}$$

where  $\mathbf{p}$  is the momentum. We can assume that this is a steady state:

$$\frac{d\mathbf{p}}{dt} = 0$$

and we can a set of equations for the steady state:

$$\begin{cases} 0 = qE_x - \omega_c p_y - \frac{p_x}{\tau} \\ 0 = qE_y + \omega_c p_x - \frac{p_y}{\tau} \end{cases}$$

where  $\omega_c = \frac{qH}{mc}$  is the cyclotron frequency. Or in terms of the conductance and resistivity:

$$\begin{cases} -\sigma_0 E_x = \omega_c \tau j_y + j_x \\ -\sigma_0 E_y = -\omega_c \tau j_x + j_y \end{cases}$$

and since  $j_y = 0$  we get

$$\begin{aligned} -\sigma_0 E_x &= j_x; & \sigma_0 &= -\frac{j_x}{E_x}, \\ -\sigma_0 E_y &= -\omega_c \tau j_x; & E_y &= \frac{\omega_c \tau}{\sigma_0} j_x \end{aligned}$$

substituting back into the Hall coefficient we get

$$\begin{aligned} R_H &= \frac{E_y}{j_x H} = \frac{\omega_c \tau}{\sigma_0 H} = \frac{q \tau}{m c \sigma_0} \\ \text{using } \sigma_0 &= n \frac{q^2 \tau}{m} \\ R_H &= \frac{1}{n c q} \end{aligned}$$

## Chapter 7: Energy Bands

For a free electron, we know that the energy is quadratic i.e.  $\epsilon \propto k^2$ . We have a boundary condition for each states  $2\pi/L$  and the energy is quantized. Some definitions

- Metal: continuous filled energy bands
- Insulator: an unfilled energy band
- Energy band gap  $E_g$
- Metal:  $E_g \rightarrow 0$
- Semi metal:  $E_g < 0.4$  eV
- Semi conductor:  $E_g \approx 0.1 \rightarrow 4$  eV
- Insulator:  $E_g > 4$  eV

insert book fig 2 chp 7 For the unperturbed case, we have a free electron with energy

$$E_k = \frac{\hbar^2 k^2}{2m} (k_x^2 + k_y^2 + k_z^2), \quad k_x, k_y, k_z = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots$$

and wavefunction

$$\psi_k(\gamma) = e^{i\mathbf{k}\cdot\gamma}$$

we have a plane wave with the Bragg condition

$$(\mathbf{k} + \mathbf{G})^2 = k^2 \implies k = \pm G/2$$

where the  $\mathbf{G}$  vector is the reciprocal lattice vector  $\mathbf{G} = 2\pi/a$ . The most scattered wave is  $k = \pm\pi/a$ , and we get two solutions as a linear combination,

$$\psi = e^{ikx} \pm e^{-ikx}$$

We can substitute for when  $k = \pm\pi/a$  for the standing waves and we get

$$\begin{aligned} \psi(+) &= 2 \cos\left(\frac{\pi}{a}x\right) \\ \psi(-) &= i2 \sin\left(\frac{\pi}{a}x\right) \end{aligned}$$

We can then define the corresponding probability density.

$$\begin{aligned} |\psi(+)|^2 &\propto \cos^2\left(\frac{\pi}{a}x\right) \\ |\psi(-)|^2 &\propto \sin^2\left(\frac{\pi}{a}x\right) \end{aligned}$$

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## 8 Lecture 2/20/24

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### Chapter 7: Cont'd

The first order energy difference is

$$\begin{aligned} E_g &= \int_0^1 dx U(x) [|\psi(+)|^2 - |\psi(-)|^2] \\ &= 2 \int_0^1 dx U(x) \cos\left(\frac{2\pi}{a}x\right) \left(\cos^2\left(\frac{2\pi}{a}x\right) - \sin^2\left(\frac{2\pi}{a}x\right)\right) \\ &= U \end{aligned}$$

This is equal to the Fourier component of the crystal potential:

$$U = U_o + U_1 \cos\left(\frac{2\pi}{a}x\right) + U_2 \cos\left(\frac{4\pi}{a}x\right) + \dots$$

**Bloch Theorem** A constraint on the wavefunction as it is a periodic function:

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

where  $u(\mathbf{r} + na) = u(\mathbf{r})$  is the periodic part of the wavefunction.  $k$  is like a quantum number where it represents the crystal momentum.

**Simple proof:** (not accurate, take a look at Ashcroft and Mermin) Given a wavefunction

$$\psi(x + a) = C\psi(x)$$

where  $a$  is the lattice constant and  $C$  is a constant or eigenvalue in the formal case. The *Periodic boundary condition* (Born-Karman) we have a ring with  $N$  lattice points so

$$\begin{aligned} \psi(x + Na) &= \psi(x) \\ C^N \psi(x) &= \psi(x) \implies C^N = 1 \\ \implies C &= e^{i2\pi s/N}; \quad s = 0, 1, 2, \dots, N-1 \\ \implies \psi(x) &= u_k(x) e^{i2\pi s x / Na} \end{aligned}$$

where

$$\frac{2\pi}{a} \frac{s}{N}$$

is the  $k$  vector. So we don't need to solve the whole equation, but rather just the periodic part  $u_k(x)$ . But true materials are not perfect crystals or harmonic potentials, so we have to solve the Schrodinger (wave) equation for the crystal potential.

$$mc^2\tau/N1$$

remember this???

**Kronig-Penney Model** We have a periodic finite potential well where the height of the potential is  $U_o$ , and in the region  $0 < x < a$  we have a potential well  $U = 0$  and in the region  $-b < x < 0$  we have a barrier  $U = U_o$  that is periodic. From the wave equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi$$

where  $\epsilon$  is the eigenenergy. For the first region:

$0 < x < a$ ,  $U = 0$  the general solution is the linear combination

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

where the energy is only kinetic:

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

$-b < x < 0$ ,  $U = U_o$  which is constant, which is renormalized::

$$\psi(x) = C e^{Qx} + D e^{-Qx}$$

where there is no  $i$  in the exponent since the plane wave is not oscillatory, but decays.

$$U_o - \epsilon = \frac{\hbar^2 Q^2}{2m}$$

at the boundary  $x = 0$ , the wavefunction and the derivative must be continuous:

$$\begin{aligned} A + B &= C + D \\ ik(A - B) &= Q(C - D) \end{aligned}$$

Using Bloch's theorem, we know that each potential barrier is the same, but with a phase shift:

$$\psi(a < x < a + b) = \psi(-b < x < 0) e^{ik(a+b)}$$

we get the continuity condition:

$$\begin{aligned} Ae^{ika} + Be^{-ika} &= (Ce^{-Qb} + De^{Qb}) e^{ik(a+b)} \\ ik[Ae^{ika} - Be^{-ika}] &= Q[Ce^{-Qb} - De^{Qb}] e^{ik(a+b)} \end{aligned}$$

with four equations and four unknowns, we can solve for the energy eigenvalues. To solve for the energy eigenvalues, we can use the determinant of the matrix of the coefficients of the equations.

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ ik & -ik & -Q & Q \\ e^{ika} & e^{-ika} & -e^{-Qb+ik(a+b)} & -e^{Qb+ik(a+b)} \\ ike^{ika} & -ike^{-ika} & -Qe^{-Qb+ik(a+b)} & Qe^{Qb+ik(a+b)} \end{pmatrix}$$

and the solution is

$$\left[ \frac{Q^2 - K^2}{2Qk} \right] \sinh(Qb) \sin(Ka) + \cosh(Qb) \cos(ka) = \cos(k(a+b))$$

we can simplify this equation for  $b \rightarrow 0$ ,  $U_o \rightarrow \infty$ : so

$$\frac{Q^2 \cdot ba}{2} = P$$

where  $Q \gg K$  and  $Qb \ll 1$  from

$$\begin{aligned} U_o - \epsilon &= \frac{\hbar^2 Q^2}{2m} \\ Q &= \sqrt{\frac{2m(U_o - \epsilon)}{\hbar^2}} \end{aligned}$$

thus

$$\frac{P}{Ka} \sin(Ka) + \cos(Ka) = \cos(ka)$$

The only allowed states are between  $-1$  and  $1$  since  $\cos ka$  has a range of  $-1$  to  $1$ . We can also think of this as a band structure where the allowed states are the energy bands and the grey areas are the forbidden states.

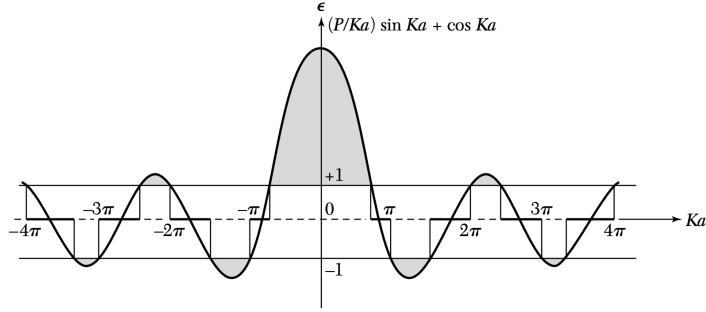


Figure 8.1: The allowed states are where the  $1 > \epsilon > 0$

**1D Case** from the Schrödinger equation for a periodic potential:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi$$

where  $U(x+a) = U(x)$  is the periodic potential which can be expanded in a Fourier series:

$$U(x) = \sum_G U_G e^{iGx}$$

so

$$\left( -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \sum_G U_G e^{iGx} \right) \psi(x) = \epsilon\psi$$

the wavefunction can be expanded in a Fourier series:

$$\psi(x) = \sum_k C_k e^{ikx} \quad k = \frac{2\pi n}{L}$$

so we can substitute this into the Schrödinger equation:

$$\begin{aligned} \left[ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \sum_G U_G e^{iGx} \right] \sum_k C_k e^{ikx} &= \epsilon \sum_k C_k e^{ikx} \\ \frac{\hbar^2}{2m} \sum_k k^2 C_k e^{ikx} + \sum_{G,k} U_G C_k e^{i(k+G)x} &= \epsilon \sum_k C_k e^{ikx} \end{aligned}$$

## Chapter 2: Wave Diffraction and the Reciprocal Lattice

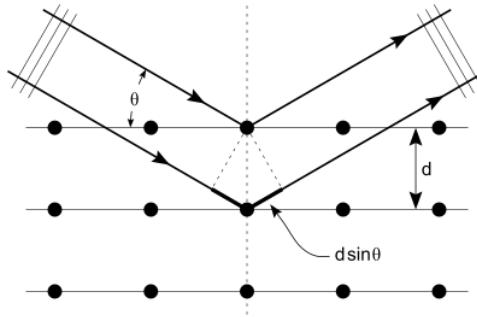


Figure 8.2: Bragg's Law

**Scattering and Bragg's Law** When two beams of same phase meet, they constructively interfere. When they are out of phase, they destructively interfere. The location of constructive interference, or path difference, is shown by the bold lines in Figure 8.2. The path difference is

$$2d \sin \theta = n\lambda$$

known as Bragg's Law which is only valid for  $\lambda \leq 2d$ . In reality each lattice plane will reflect about  $10^{-3} \sim 10^{-5}$  of the incident beam. Thus only about  $10^3 \sim 10^5$  planes contribute to the diffraction. The periodicity of the lattice leads to a periodic observable...

*aside:* The electron wavefunction is not observable— $\psi$  is a complex number, but the electron density,  $\psi^* \psi$ , is observable. Read about the quantized Hall effect (Queen):) and Superconductivity (King).

$$\psi(x + T) = \psi(x) e^{i\theta} n(x + T) = n(x)$$

**Fourier Transform** The discrete Fourier transform is useful for periodic functions.

$$\begin{aligned} n(x) &= \sum_{p \geq 0} \left[ C_p \cos\left(\frac{2\pi}{a}x\right) + S_p \sin\left(\frac{2\pi}{a}x\right) \right] \\ &= \sum_p n_p e^{i\frac{2\pi}{a}px} \end{aligned}$$

or in vector notation

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_G e^{i\mathbf{G} \cdot \mathbf{r}}$$

Since  $n(x)$  is real, there is a symmetry of the complex conjugate

$$n_p = n_{-p}^*$$

### Inverse Fourier Transform

$$n_p = \frac{1}{a} \int_0^a n(x) e^{-i\frac{2\pi}{a}px} dx$$

and in vector notation

$$n_G = \frac{1}{V} \int_{cell} n(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} dV$$

**Reciprocal Space Vectors** The basis vectors of the reciprocal lattice are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

where the denominator is the volume of the unit cell (parallelepiped)  $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = V_c$ . Taking the dot product of a primitive vector with a reciprocal lattice vector gives

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

where the Kronecker delta tells us that the dot product is either  $2\pi$  or 0. With this we can write the  $\mathbf{G}$  vector as a linear combination of the reciprocal lattice vectors

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

we can also show that

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

which means that this is invariant under translations.

### Scattering amplitude

$$F = \int d\mathbf{r} n(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}}$$

where  $|\mathbf{k}| = |\mathbf{k}'|$ . In vector notation

$$\begin{aligned} F &= \int d\mathbf{r} \sum_{\mathbf{G}} n_G e^{i(\mathbf{G} - \mathbf{r}') \cdot \mathbf{r}} e^{-i\Delta\mathbf{k} \cdot \mathbf{r}} \\ &= \sum_{\mathbf{G}} n_G \int d\mathbf{r} e^{i(\mathbf{G} - \Delta\mathbf{k}') \cdot \mathbf{r}} \end{aligned}$$

where  $\Delta\mathbf{k} = -(\mathbf{k} - \mathbf{k}')$ . When  $\mathbf{G} = \Delta\mathbf{k}$  we can rewrite to

$$\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$$

in absolute value

$$|\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}'| \rightarrow |\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}| \rightarrow |\mathbf{k} + \mathbf{G}| = |\mathbf{k}|$$

and

$$(\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G}) = \mathbf{k} \cdot \mathbf{k} \rightarrow 2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0$$

For the 1D crystal  $G = 2\pi/a$ . Since  $\mathbf{k} \cdot \mathbf{G} = 2\pi/\lambda G \sin \theta$  and  $2\mathbf{k} \cdot \mathbf{G} = \mathbf{G}^2$  We get

$$\begin{aligned} 2 \cdot \frac{2\pi}{\lambda} G \sin \theta &= \mathbf{G}^2 \\ \rightarrow \frac{4\pi}{\lambda} \sin \theta &= G \end{aligned}$$

since  $G = 2\pi/a$  we get Bragg's Law

$$2d \sin \theta = n\lambda$$

For the SC the reciprocal lattice is SC, but for BCC, the reciprocal lattice is different...

## Chapter 2: cont'd

**Wigner-Seitz primitive cell:** How to create the most symmetric primitive cell.

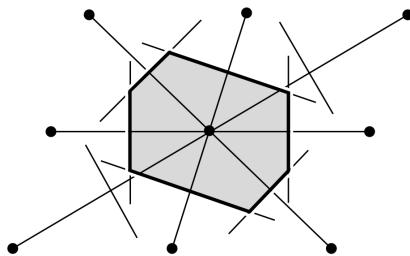


Figure 8.3: Wigner-Seitz Primitive Cell

Steps: Connect a given lattice point to all nearby lattice points. Bisect all lines. The area enclosed by the bisectors is the Wigner-Seitz primitive cell as shown in Figure 8.3.

**Reciprocal Lattice of SC** The lattice vectors (primitive translation vectors) are

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}}$$

the reciprocal lattice vectors using the formula from last lecture are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_c} = \frac{2\pi}{a} \hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a} \hat{\mathbf{z}}$$

**Reciprocal Lattice of BCC** The lattice vectors are

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

and the reciprocal lattice vectors are

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

**Reciprocal Lattice of FCC** The lattice vectors are

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

which is the same as the reciprocal space of BCC. Thus, the reciprocal lattice of FCC is BCC!

**Brillouin Zone** The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice.

## Chapter 3: Crystal Binding and Elastic Constants

We are mostly interested in the E&M interaction between atoms on the energy scale of eV (e.g. the band gap of silicon is 1.2 eV).

**There are 4 main types of bonds:**

**Metallic Bond** Bonds between metals have weakly bound valence electrons. Hence the electrons move freely around like a fluid. This is why metals are good conductors.

**Ionic Bond** Bonds between metals and non-metals (e.g. NaCl). The opposing charges attract each other where the electrons form full shells and hence less conductivity.

**Covalent Bond** Bonds between non-metals (e.g. Si). The atomic orbitals defined by QM describes the bonds through the hybridization of the orbital wavefunctions (e.g.  $sp^3$  in diamond). This is a very difficult problem to solve.

**Van der Waals interaction** Inert gases... e.g. He is interesting as it is a liquid at very low temperatures, and it is a boson (He-4 superfluid) and fermion (He-3) depending on the number of neutrons.

**Hydrogen Bonding** is very important in biology, but not in solid state physics.

### Van der Waals interaction

Two types of energy to consider:

- Cohesive energy: Energy required to separate bound atoms. The cohesive energy of a solid is the sum of the cohesive energies of the bonds.
- Ionization energy: Energy required to remove an electron from an atom.

The ionization energy is larger because the Van der Waals interaction is a weaker bond. Given two inert gas atoms, there is no dipole or charge distribution contributing to the interactions between the atoms. In QM, there is no zero point energy, so we have to consider the atoms to not be perfect, but rather vibrate around a mean position. This is a dipole-dipole interaction.

**dipole-dipole** Given two electrons spaced by a distance  $R$  in a 1D lattice, one atom fluxuates by  $x_2$  and the other by  $x_1$ . The Hamiltonian of the unperturbed system is

$$H_o = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2$$

The Coulomb interaction:

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

Using Taylor expansion (2nd order) for small  $x_1$  and  $x_2$  we get

$$H_1 = -\frac{2e^2}{R^3}x_1x_2$$

Since this has 2 degrees of freedom, we have a 2x2 matrix with 2 eigenvalues diagonalized by the normal mode transform. This results in 2 Canconical Modes:

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2) \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2)$$

THe total Hamiltonian is

$$\begin{aligned} H &= \frac{1}{2m} \left[ \frac{1}{2}(p_s + p_a)^2 \right] + \frac{1}{2m} \left[ \frac{1}{2}(p_s - p_a)^2 \right] - 2\frac{e^2}{R^3} \cdot \frac{1}{2}(x_s^2 - x_a^2) + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2 \\ &= \left[ \frac{p_s}{2m} + \frac{1}{2} \left( c - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[ \frac{p_a}{2m} + \frac{1}{2} \left( c + \frac{2e^2}{R^3} \right) x_a^2 \right] \end{aligned}$$

1. For the HCP structure ABAB... the atoms in the B layer are equidistant from the atoms in the lower basal plane. The distance between an atom in the A layer and the atom in the B layer is equivalent to the distance between the atoms in the basal plane  $a$ . Also the height of the B layer is  $c/2$ . We can draw a right triangle with the hypotenuse being the distance between the atoms  $a$  and two sides of length  $c/2$  and  $x$  as shown in Figure 4.

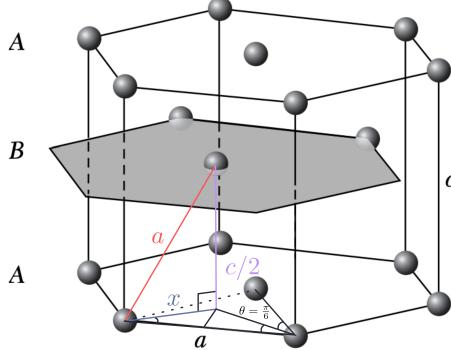


Figure 4: HCP structure (From Kittel)

To find  $x$  we can project the B atom onto the basal plane and use trig to find that

$$x \cos \frac{\pi}{6} = \frac{a}{2} \rightarrow x = \frac{a}{\sqrt{3}}$$

So using the Pythagorean theorem we can find the distance between the atoms in the A and B layers

$$\begin{aligned} a^2 &= \left(\frac{c}{2}\right)^2 + x^2 \\ a^2 &= \frac{c^2}{4} + \left(\frac{a}{\sqrt{3}}\right)^2 \\ \frac{2}{3}a^2 &= \frac{c^2}{4} \\ \frac{c}{a} &= \sqrt{\frac{8}{3}} \approx 1.633 \end{aligned}$$

2. (a) Given

$$\mathbf{a}_1 = (\sqrt{3}a/2)\hat{x} + (a/2)\hat{y}; \quad \mathbf{a}_2 = -(\sqrt{3}a/2)\hat{x} + (a/2)\hat{y}; \quad \mathbf{a}_3 = c\hat{z}$$

the volume of the primitive cell is equivalent to the volume of the parallelepiped:

$$\begin{aligned} V_c &= \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \\ &= \mathbf{a}_1 \cdot \det \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\sqrt{3}a/2 & a/2 & 0 \\ 0 & 0 & c \end{vmatrix} \\ &= \left( \frac{\sqrt{3}a}{2}\hat{x} + \frac{a}{2}\hat{y} \right) \cdot \left( \frac{ac}{2}\hat{x} + \frac{\sqrt{3}ac}{2}\hat{y} \right) \\ &= \frac{\sqrt{3}a^2c}{4} + \frac{\sqrt{3}a^2c}{4} \\ &= \frac{\sqrt{3}a^2c}{2} \end{aligned}$$

(b) The first reciprocal lattice vector is

$$\begin{aligned}\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_c} \\ &= 2\pi \frac{\left(\frac{ac}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}ac}{2}\hat{\mathbf{y}}\right)}{\frac{\sqrt{3}a^2c}{2}} \\ &= 2\pi \frac{\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}}{\sqrt{3}a} \\ &= \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}\hat{\mathbf{x}} + \hat{\mathbf{y}} \right)\end{aligned}$$

The other reciprocal lattice vectors can be found similarly:

$$\mathbf{a}_3 \times \mathbf{a}_1 = \det \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 0 & 0 & c \\ \sqrt{3}a/2 & a/2 & 0 \end{vmatrix} = -\frac{ac}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}ac}{2}\hat{\mathbf{y}}$$

so

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_c} = \frac{2\pi}{a} \left( -\frac{1}{\sqrt{3}}\hat{\mathbf{x}} + \hat{\mathbf{y}} \right)$$

and

$$\mathbf{a}_1 \times \mathbf{a}_2 = \det \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ \sqrt{3}a/2 & a/2 & 0 \\ -\sqrt{3}a/2 & a/2 & 0 \end{vmatrix} = (\sqrt{3}a^2/4 + \sqrt{3}a^2/4)\hat{\mathbf{z}} = \frac{\sqrt{3}a^2}{2}\hat{\mathbf{z}}$$

so

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_c} = \frac{2\pi}{c}\hat{\mathbf{z}}$$

(c) A sketch of the 2D Brillouin zone is a hexagon as shown in Figure 5.

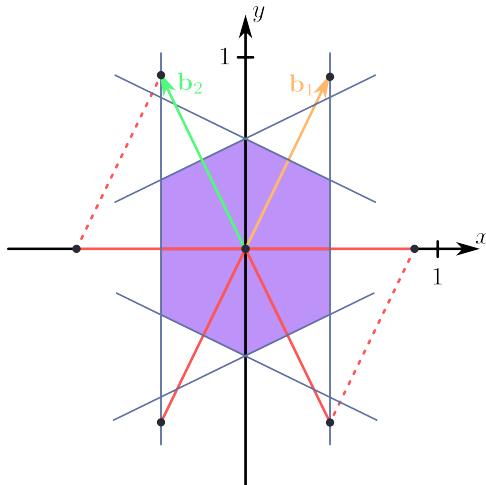


Figure 5: 2D Brillouin zone on  $xy$  plane

3. (a) The total potential energy is

$$U(R) = N \left( \frac{A}{R^n} - \frac{\alpha q^2}{R} \right)$$

where the Madelung constant for a 1D chain of ions is  $\alpha = 2 \ln 2$ , and we replace the usual repulsive potential  $\lambda \exp(-R/p)$  with  $A/R^n$ . Taking the derivative with respect to  $R$  and finding the equilibrium separation at a critical point:

$$\begin{aligned}\frac{dU}{dR} &= N \left( -\frac{nA}{R^{n+1}} + \frac{\alpha q^2}{R^2} \right) = 0 \\ \frac{NA}{R^{n+1}} &= \frac{\alpha q^2}{R^2} \\ \frac{R^{n+1}}{R^2} &= \frac{nA}{\alpha q^2} \\ R_o^{n-1} &= \frac{nA}{\alpha q^2} \\ A &= \frac{\alpha q^2 R_o^{n-1}}{n}\end{aligned}$$

substituting back into the potential energy:

$$\begin{aligned}U(R_o) &= N \left( \frac{\alpha q^2 R_o^{n-1}}{n R_o^n} - \frac{\alpha q^2}{R_o} \right) \\ &= N \left( \frac{\alpha q^2}{n R_o} - \frac{\alpha q^2}{R_o} \right) \\ &= \frac{N \alpha q^2}{R_o} \left( \frac{1}{n} - 1 \right) \\ U(R_o) &= -\frac{2Nq^2 \ln 2}{R_o} \left( 1 - \frac{1}{n} \right)\end{aligned}$$

(b) Approximating the potential around  $x$  using Taylor expansion  $f(x+h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2$ :

$$\begin{aligned}U(R_o(1-\delta)) &= U(R_o + (-R_o\delta)) \\ &= U(R_o) - [U'(R_o)](R_o\delta) + \frac{1}{2}[U''(R_o)](R_o\delta)^2 + \dots\end{aligned}$$

and since  $\frac{dU}{dR} = 0$  at  $R_o$ , the second term is zero. And the second order derivative gives

$$\begin{aligned}\frac{d^2U}{dR^2} &= N \left( \frac{n(n+1)A}{R^{n+2}} - \frac{2\alpha q^2}{R^3} \right) \Big|_{R=R_o} \\ \text{using } R_o^{n-1} &= \frac{nA}{\alpha q^2} \\ &= N \left( \frac{n(n+1)A}{\frac{nA}{\alpha q^2} R_o^3} - \frac{2\alpha q^2}{R_o^3} \right) \\ &= N \left( \frac{(n+1)\alpha q^2}{R_o^3} - \frac{2\alpha q^2}{R_o^3} \right) \\ &= \frac{N\alpha q^2}{R_o^3} ((n+1) - 2) \\ \frac{d^2U}{dR^2} &= \frac{N\alpha q^2}{R_o^3} (n-1)\end{aligned}$$

so potential is approximately

$$U(R_o(1-\delta)) \approx U(R_o) + \frac{1}{2} \frac{N\alpha q^2}{R_o^3} (n-1)(R_o\delta)^2$$

so the leading coefficient is (ignoring the  $\frac{1}{2}\delta^2$  part)

$$C = \frac{N\alpha q^2}{R_o^3} (n - 1) R_o^2$$

To cancel the  $N$  we can use that fact that compressing to the unit length makes the separation between ions  $2NR_o = 1$ , so  $N = 1/(2R_o)$ , so

$$C = \frac{1}{2R_o} \frac{\alpha q^2}{R_o^3} (n - 1) R_o^2 = \frac{\alpha q^2}{2R_o^2} (n - 1)$$

and using the Madelung constant  $\alpha = 2 \ln 2$ , the leading term is finally

$$C = \frac{(n - 1)q^2 \ln 2}{R_o^2}$$

so the work done is

$$\begin{aligned} W &= \Delta U = U((R_o\delta)) - U(R_o) \\ &\approx U(R_o) + \frac{1}{2}C\delta^2 - U(R_o) \\ W &\approx \frac{1}{2}C^2\delta^2 \end{aligned}$$

where the leading term is indeed in the order of  $\frac{1}{2}C\delta^2$ .