

# Solid State Physics

Theory of Metal

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## —Basic Notion—

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- 1-2 Fourier Transform on Bravais Lattice
- 1-3 Reciprocal Lattice Vector
- 1-4 Brillouin Zone

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- Appendix – Lifetime of Quasiparticles at Finite Temperature

## —Preface—

### **Basic Concepts**

The electronic properties of a crystal can be characterized by the followings:

In real space:

- Unit cell Chap 1-1
- Electron density

In momentum space:

- Energy band structure (energy levels as a function of wave vector) Chap 2-2, 4-1, 5-2
- Fermi surface (locus of points with Fermi energy in the first Brillouin zone) Chap 5-2
- Density of states (the number of states in the energy interval) Chap 3-3, 4-3, 5-3

### **Academic Years of Lecture**

- 2014 Fall - 2015 Spring
- 2015 Fall - 2016 Spring
- 2016 Fall - 2017 Spring
- 2021 Fall - 2022 Spring
- 2022 Fall - 2023 Spring
- 2023 Fall - 2024 Spring

- ❖ The latest version is available at  
[web.phy.ntnu.edu.tw/~hongyi/?url=lecture](http://web.phy.ntnu.edu.tw/~hongyi/?url=lecture)

## —Bibliography—

### **Graduate Level**

Prerequisite Knowledge: Quantum Mechanics, Statistical Mechanics

1. N. W. Ashcroft & N. D. Mermin, *Solid State Physics* (Saunders College).
2. Yuri Galperin, *Introduction to Modern Solid State Physics* (CreateSpace Independent Publishing Platform).
3. J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press).
4. This Condensed Life.  
<https://thiscondensedlife.wordpress.com/archives/>
5. Theoretical Physics Reference.  
<http://www.theoretical-physics.net/dev/index.html>

### **Undergraduate Level**

Prerequisite Knowledge: Quantum Mechanics

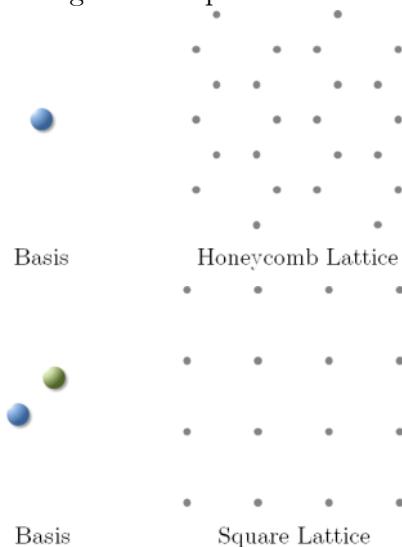
1. Charles Kittle, *Introduction to Solid State Physics* (John Wiley & Sons).
2. Steven H. Simon, *The Oxford Solid State Basics* (Oxford University Press).

# 1-1 Bravais Lattice

Tuesday, December 20, 2011 8:22 PM

## A. CRYSTAL

- (1) A crystal is made up by a basis putting on an infinite regular arrangement of points referred to as lattice sites.



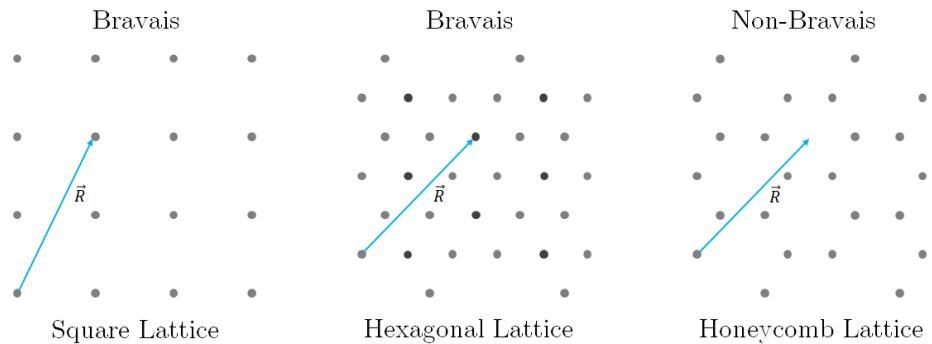
- (2) Lattice sites don't tell you the position of an atom in a crystal. They are simply points 'in space' oriented in such a way to build a crystal.

## B. BRAVAIS [bravei] LATTICE (1850)

- (1) A Bravais lattice is a regular periodic arrangement of points in space all of them *connected* by translation vectors,  
OS:

Mathematically, any point in an infinite lattice can be considered as an origin.

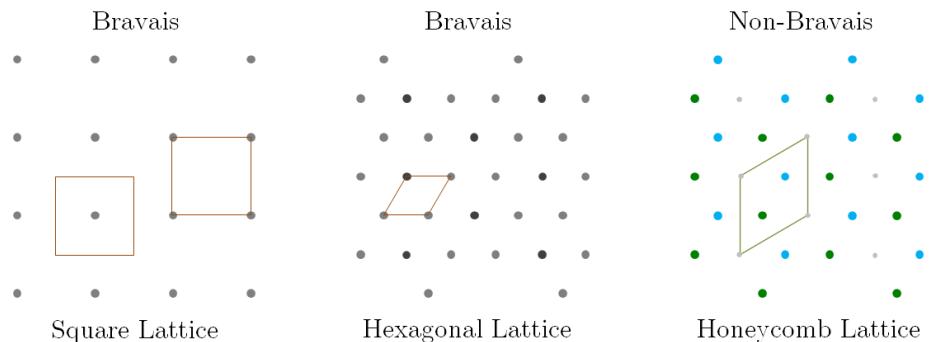
$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ , where  $\vec{a}_1, \vec{a}_2$  and  $\vec{a}_3$  are primitive vectors, and  $n_1, n_2$  and  $n_3$  are arbitrary integers.



- (2) In other word, the neighborhood of any Bravais lattice point remaining the same as any other point under a translation.

### C. UNIT CELL

- (1) For examples, both the square lattice and hexagonal lattice are Bravais lattices. In order to categorized Bravais lattices, consider a simplest repeating unit in a lattice is called a unit cell. A unit cell contains precisely one Bravais lattice point.



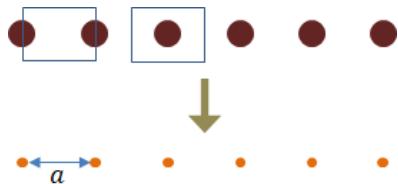
- (2) Lattice constant: the length of the primitive vector

$$\begin{aligned}|\vec{a}_1| &= a \\ |\vec{a}_2| &= b \\ |\vec{a}_3| &= c\end{aligned}$$

The volume of the unit cell is  $V_{\text{cell}} = |\vec{a}_1 \times \vec{a}_2 \cdot \vec{a}_3| = abc$

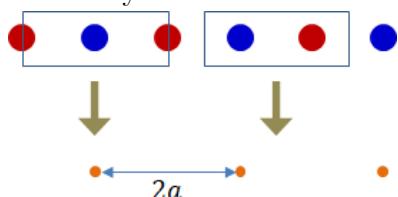
#### EXAMPLES:

- ### 1. 1D identical atoms:



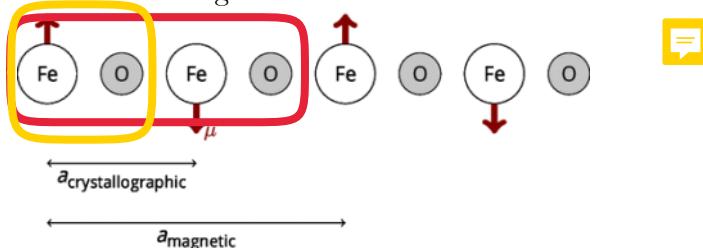
Lattice constant =  $a$

## 2. 1D binary atoms



Lattice constant =  $2a$

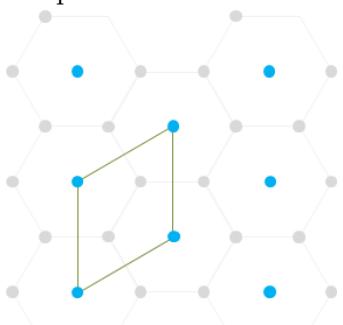
## 3. 1D antiferromagnetic chain



Nonmagnetic lattice constant =  $a = a_{\text{crystallographic}}$

Magnetic lattice constant =  $2a = a_{\text{magnetic}}$

## 4. Graphene:



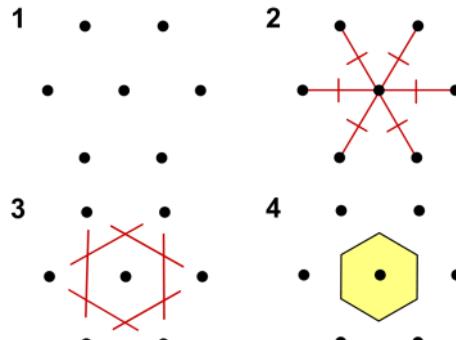
Distance between two carbons:  $a_{\text{A-B}} = 0.142 \text{ nm}$

Lattice constant =  $\sqrt{3}a_{\text{A-B}}$

## (3) Wigner-Seitz cell (1934)

A smallest possible primitive unit cell, which consist of one lattice

point and all the surrounding space closer to it than to any other point.  
CONSTRUCTION:

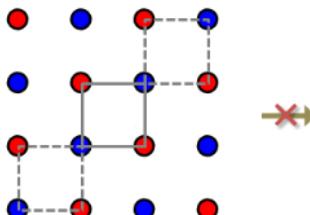


1. One chooses any lattice point and draws connecting lines to its closest neighbors.
2. One constructs the perpendicular bisectors of the connecting lines.
3. The enclosed area is the Wigner-Seitz cell.

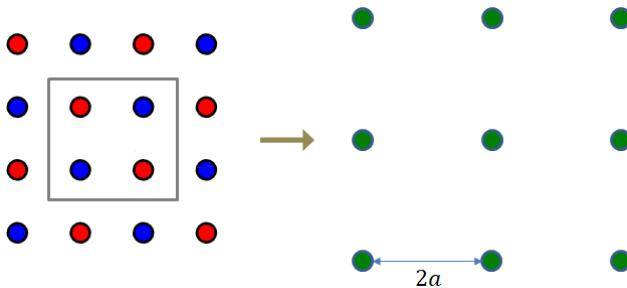
#### EXAMPLES:

1. 2D antiferromagnetic crystal:

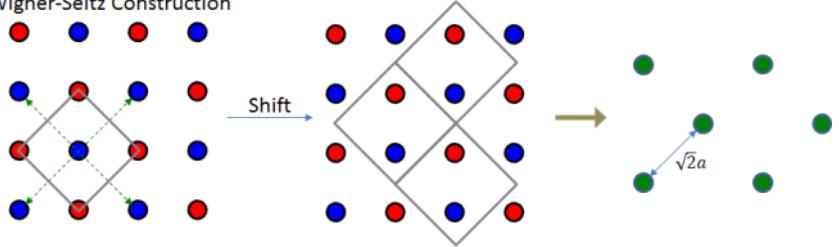
One cell contains two atoms



One cell contains four atoms



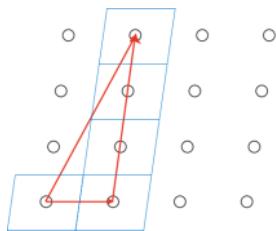
### Wigner-Seitz Construction



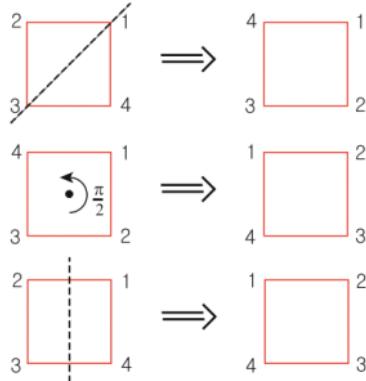
$$\text{Lattice constant: } |\vec{a}_1| = |\vec{a}_2| = \sqrt{2}a$$

- (4) Wigner-Seitz cell preserves most of the discrete symmetries.

#### 1. Discrete translation



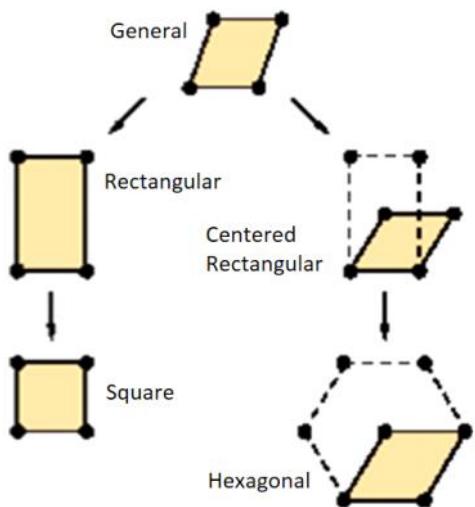
#### 2. Point group: inversion, rotation, and reflection



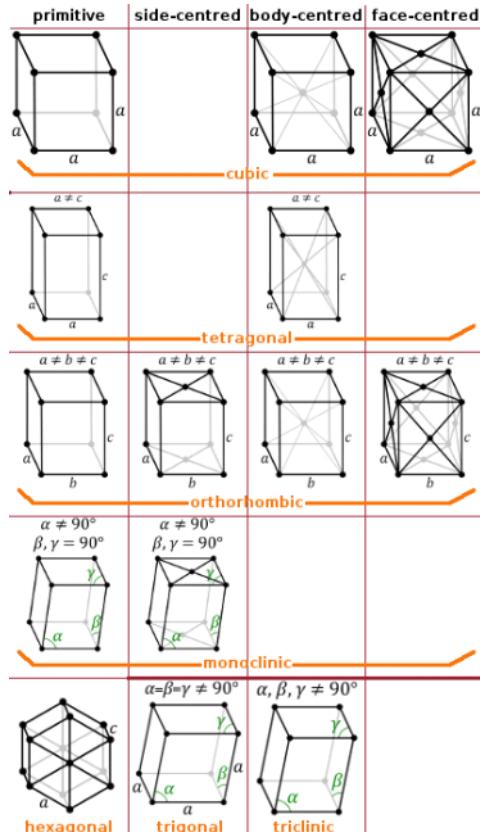
## D. CATEGORIES OF BRAVAIS LATTICES

- (1) 2D lattice

The number of Bravais lattices is limited by symmetry of the unit cell



## (2) 3D lattice

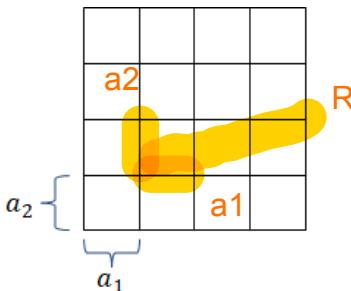


# 1-2 Fourier Transform on Bravais Lattice

2021年9月25日 上午 11:48

## A. FOURIER TRANSFORM OF A BRAVAIS LATTICE

- (1) Suppose  $f(\vec{r})$  is periodic with period  $\vec{R}$ , i.e.,  $f(\vec{r} + \vec{R}) = f(\vec{r})$  where  $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$  is the lattice vector and  $\vec{a}_i$  are primitive vectors.



Suppose that there is a large enough lattice with size  $L$ . The function  $f(\vec{r})$  is defined in the volume  $\mathcal{V} = L_1 L_2 L_3$ , and the Fourier transform over the finite volume is

$$\begin{aligned} f_k &= \frac{1}{\mathcal{V}} \int f(\vec{r} + \vec{R}) e^{-i\vec{k} \cdot (\vec{r} + \vec{R})} d^3 r \\ &= \frac{1}{\mathcal{V}} \sum_R \int_{\text{unit cell}} f(\vec{r} + \vec{R}) e^{-i\vec{k} \cdot (\vec{r} + \vec{R})} d^3 r \\ &= \frac{1}{\mathcal{V}} \sum_R e^{-i\vec{k} \cdot \vec{R}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d^3 r \end{aligned}$$

Since  $\mathcal{V} = N_{\text{cell}} \mathcal{V}_{\text{cell}}$

$$f_k = \frac{1}{N_{\text{cell}}} \sum_R e^{-i\vec{k} \cdot \vec{R}} \frac{1}{\mathcal{V}_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d^3 r$$

$$\begin{aligned}
\sum_R e^{-i\vec{k}\cdot\vec{R}} &= \sum_{n_1, n_2, n_3} e^{-i\vec{k}\cdot(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3)} \\
&= \prod_i \sum_{n_i} e^{-i\vec{k}\cdot\vec{a}_i n_i} \\
&= \prod_i \sum_{n_i} (e^{-i\vec{k}\cdot\vec{a}_i})^{n_i}
\end{aligned}$$

Since  $L_i = N_i a_i$

$$\sum_{n_i=0}^{N_i-1} (e^{-i\vec{k}\cdot\vec{a}_i})^{n_i} = \frac{1 - (e^{-i\vec{k}\cdot\vec{a}_i})^{N_i}}{1 - e^{-i\vec{k}\cdot\vec{a}_i}} = \frac{1 - e^{-i\vec{k}\cdot\vec{a}_i N_i}}{1 - e^{-i\vec{k}\cdot\vec{a}_i}} = \frac{1 - e^{-i\vec{k}\cdot\vec{L}_i}}{1 - e^{-i\vec{k}\cdot\vec{a}_i}}$$

Since  $\vec{k} \cdot \vec{L}_i = 2\pi\ell_i$

$$\sum_{n_i=0}^{N_i-1} (e^{-i\vec{k}\cdot\vec{a}_i})^{n_i} = \frac{1 - 1}{1 - e^{-i\vec{k}\cdot\vec{a}_i}} = \frac{0}{1 - e^{-i\vec{k}\cdot\vec{a}_i}}$$

The equation above gives zero unless

$$e^{-i\vec{k}\cdot\vec{a}_i} = 1 \Rightarrow \vec{k} \cdot \vec{a}_i = 2\pi m_i$$

$$\Rightarrow \vec{k} = \frac{2\pi m_i}{\vec{a}_i} \text{ where } m_i = 0, \dots, N_i - 1$$

- (2) The distance between the nearest neighboring points in the discrete  $k$ -space is

$$\Delta k_i = \frac{2\pi}{|\vec{a}_i|} = \text{constant}$$

where  $|\vec{a}_i| = a$  is the lattice constant.

$\Rightarrow \vec{k}$  is discretized and is independent of the size of the finite system.

$\Rightarrow$  The discrete set of  $\{\vec{k}\}$  is periodic in  $k$ -space.

- (3) Similar to the real space, the periodic array of  $k$ -points can be referred to as the **reciprocal lattice**. Any point on the reciprocal lattice is given by  $\vec{k} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \equiv \vec{G}$  (reciprocal lattice vector), where  $\vec{b}_1, \vec{b}_2, \vec{b}_3$  are primitive vectors in the reciprocal lattice.

Since  $\vec{k} \cdot \vec{a}_i = 2\pi m_i \Rightarrow \vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$ .

One can construct  $\vec{b}_i$  such that they obey

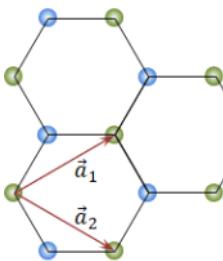
$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)} \Rightarrow \begin{cases} \vec{b}_1 = \frac{2\pi}{V_{\text{cell}}} \vec{a}_2 \times \vec{a}_3 \\ \vec{b}_2 = \frac{2\pi}{V_{\text{cell}}} \vec{a}_3 \times \vec{a}_1 \\ \vec{b}_3 = \frac{2\pi}{V_{\text{cell}}} \vec{a}_1 \times \vec{a}_2 \end{cases}$$

where  $V_{\text{cell}} = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$  is the volume of the unit cell.

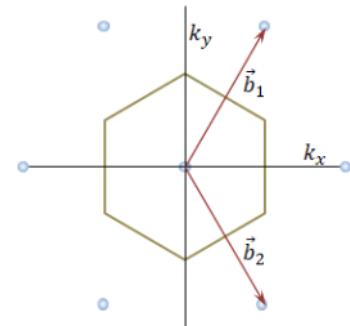
EXAMPLES:

Graphene

Real space



Reciprocal space



$$\begin{cases} \vec{a}_1 = \frac{a}{2}(3, \sqrt{3}) \\ \vec{a}_2 = \frac{a}{2}(3, -\sqrt{3}) \end{cases} \Rightarrow \begin{cases} \vec{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}) \\ \vec{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \end{cases}$$

## B. FOURIER TRANSFORM OF A PERIODIC FUNCTION IN A BRAVAIS LATTICE

- (1) Consider a function  $f(\vec{r})$  that is periodic in an infinite lattice

$$f(\vec{r}) = \int f_k e^{i\vec{k} \cdot \vec{r}} d^3 k - \sum_{k=-\infty}^{\infty} f_k e^{i\vec{k} \cdot \vec{r}}$$

becomes a Fourier series and the Fourier coefficient  $f_k$  is

$$f_k = \frac{1}{N_{\text{cell}}} \sum_R e^{-i\vec{k} \cdot \vec{R}} \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d^3 r$$

- (2) Construct a unit cell in the reciprocal lattice (called Brillouin zone, BZ)

$$f(\vec{r}) = \sum_G \sum_{k \in \text{BZ}} f_{k+G} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} = \sum_G e^{i\vec{G} \cdot \vec{r}} \sum_{k \in \text{BZ}} f_{k+G} e^{i\vec{k} \cdot \vec{r}}$$

Here,

$$\begin{aligned} \sum_{k \in \text{BZ}} f_{k+G} e^{i\vec{k} \cdot \vec{r}} &= \sum_{k \in \text{BZ}} e^{i\vec{k} \cdot \vec{r}} \frac{1}{V} \sum_R \int_{\text{unit cell}} f(\vec{r} + \vec{R}) e^{-i(\vec{k} + \vec{G}) \cdot (\vec{r} + \vec{R})} d^3 r \\ &= \frac{1}{V} \sum_{k \in \text{BZ}} \sum_R e^{-i(\vec{k} + \vec{G}) \cdot \vec{R}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r \end{aligned}$$

Since  $\sum_R e^{-i(\vec{k} + \vec{G}) \cdot \vec{R}} = \begin{cases} N_{\text{cell}} \delta_{k,G}, & \vec{k} = \ell \vec{G} \\ 0, & \vec{k} \neq \ell \vec{G} \end{cases}$  where  $\ell = 0, 1, 2, \dots, \infty$

$$\begin{aligned} \Rightarrow \sum_{k \in \text{BZ}} f_{k+G} e^{i\vec{k} \cdot \vec{r}} &= \frac{N_{\text{cell}}}{V} \sum_{k \in \text{BZ}} \delta_{k,G} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r \\ &= \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r \end{aligned}$$

$$f(\vec{r}) = \sum_G e^{i\vec{G} \cdot \vec{r}} \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r$$

- (3) Since  $\vec{k} = \ell \vec{G}$  and, without loss of generality, let  $\ell = 1$ , the Fourier coefficients become

$$f_k \rightarrow f_G = \frac{1}{N_{\text{cell}}} \sum_R e^{-i\vec{G} \cdot \vec{R}} \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r$$

$$\sum_R e^{-i\vec{G} \cdot \vec{R}} = \sum_R e^{-i(m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3) \cdot (n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3)}$$

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

$$\Rightarrow \sum_R e^{-i\vec{G} \cdot \vec{R}} = \sum_R e^{-i2\pi(n_1 m_1 + n_2 m_2 + n_3 m_3)}$$

Let  $m = n_1 m_1 + n_2 m_2 + n_3 m_3$  be an integer number.

$$\Rightarrow \sum_R e^{-i\vec{G} \cdot \vec{R}} = \sum_R e^{-i2\pi m} = \sum_R 1 = N_{\text{cell}}$$

$$f_G = \frac{1}{N_{\text{cell}}} N_{\text{cell}} \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r$$

$$= \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r$$

$$\Rightarrow \boxed{f(\vec{r}) = \sum_G f_G e^{i\vec{G} \cdot \vec{r}}}$$

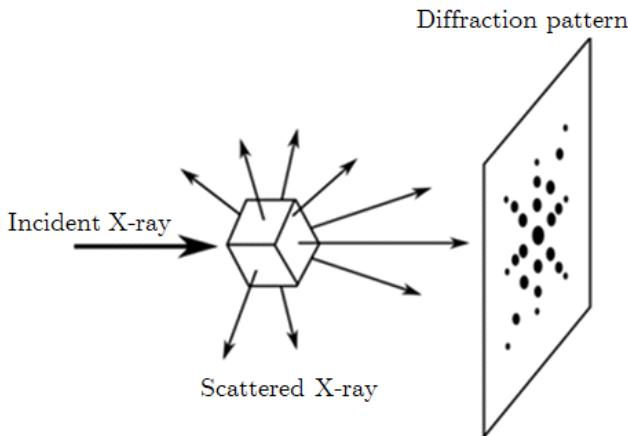
Any function  $f(\vec{r})$  that is periodic in an infinite lattice can be expanded in a Fourier series of the reciprocal lattice vector  $\vec{G}$ .

# 1-3 Reciprocal Lattice Vector

Tuesday, May 14, 2013 4:08 PM

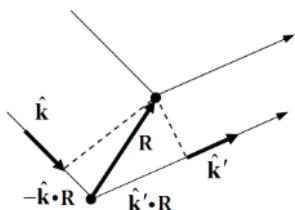
## A. PHYSICAL INTERPRETATION OF RECIPROCAL LATTICE VECTORS

- (1) X-ray diffraction (XRD) (1912):



- (2) Laue's explanation (1912):

Consider two scatterers (real lattice sites) separated by a lattice translation vector  $\vec{R}$ .



Constructive interference occurs when the path difference between the X-ray scattered from the two scatterers is

$$(\hat{\mathbf{k}}' - \hat{\mathbf{k}}) \cdot \vec{R} = n\lambda$$

As the scattering is elastic, i.e., the wavelength of the incident and the scattered X-ray is the same as  $\lambda$ .

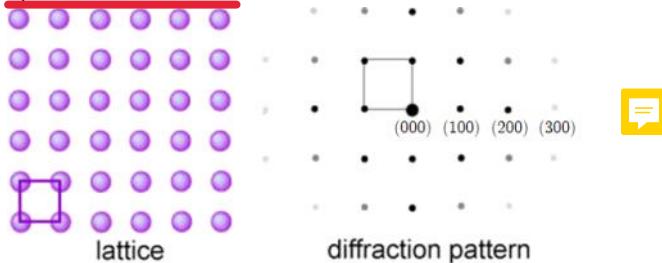
$$\vec{\mathbf{k}} = \frac{2\pi \hat{\mathbf{k}}}{\lambda} \text{ and } \vec{\mathbf{k}}' = \frac{2\pi \hat{\mathbf{k}}'}{\lambda}$$

$$\frac{2\pi}{\lambda}(\vec{k}' - \vec{k}) \cdot \vec{R} = \frac{2\pi}{\lambda}n\lambda \Rightarrow (\vec{k}' - \vec{k}) \cdot \vec{R} = 2\pi n$$

Since  $\vec{G} \cdot \vec{R} = 2\pi n$

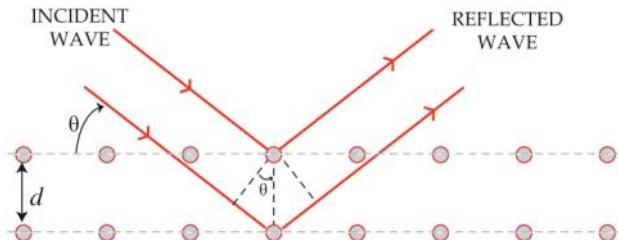
$\Delta\vec{k} = \vec{k}' - \vec{k} = \vec{G}$ .....Laue's condition

⇒ Each reciprocal lattice point defined by  $\vec{G}$  represents a diffraction spot on the screen.



(3) Bragg's explanation (Bragg's law, 1912):

A crystal is made out of parallel planes of atoms spaced by distance  $d$ .



Constructive interference occurs when the path difference is an integral number of wave length  $\lambda$ , i.e.,  $2d \sin \theta = n\lambda$

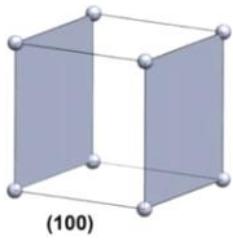
(4) The parallel planes of atoms are described by Miller indices (1839).

Find the Miller indices:

1. Determine the intersection of the plane with primitive vectors as  $(n_1, n_2, n_3)$ .
2. Take the reciprocals of the intercepts  $(1/n_1, 1/n_2, 1/n_3)$ .
3. If fractions result, multiply each by the denominator of the smallest fraction.
4. Refers to a family of parallel planes labeled as  $(hkl)$ .

#### EXAMPLES:

1. Simple cubic

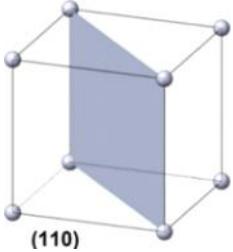


Intercepts:

$$n_1 = 1, n_2 = \infty, n_3 = \infty$$

Reciprocals:

$$\left( \frac{1}{n_1}, \frac{1}{n_2}, \frac{1}{n_3} \right) = \left( \frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty} \right) = (1,0,0)$$

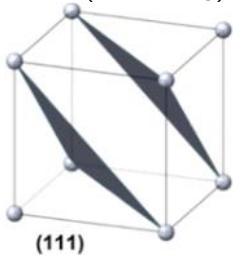


Intercepts:

$$n_1 = 1, n_2 = 1, n_3 = \infty$$

Reciprocals:

$$\left( \frac{1}{n_1}, \frac{1}{n_2}, \frac{1}{n_3} \right) = \left( \frac{1}{1}, \frac{1}{1}, \frac{1}{\infty} \right) = (1,1,0)$$



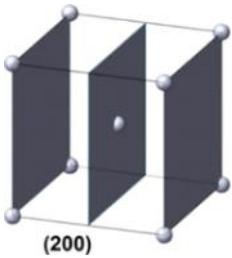
Intercepts:

$$n_1 = 1, n_2 = 1, n_3 = 1$$

Reciprocals:

$$\left( \frac{1}{n_1}, \frac{1}{n_2}, \frac{1}{n_3} \right) = \left( \frac{1}{1}, \frac{1}{1}, \frac{1}{1} \right) = (1,1,1)$$

2. Body-center cubic

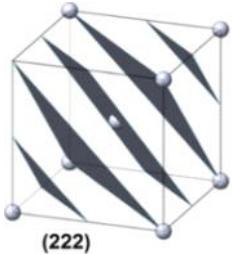


Intercepts:

$$n_1 = \frac{1}{2}, n_2 = \infty, n_3 = \infty$$

Reciprocals:

$$\left( \frac{1}{n_1}, \frac{1}{n_2}, \frac{1}{n_3} \right) = \left( \frac{1}{\frac{1}{2}}, \frac{1}{\infty}, \frac{1}{\infty} \right) = (2,0,0)$$



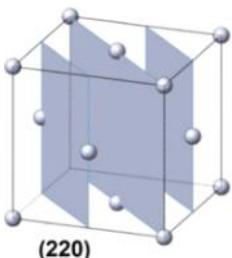
Intercepts:

$$n_1 = \frac{1}{2}, n_2 = \frac{1}{2}, n_3 = \frac{1}{2}$$

Reciprocals:

$$\left( \frac{1}{n_1}, \frac{1}{n_2}, \frac{1}{n_3} \right) = \left( \frac{1}{\frac{1}{2}}, \frac{1}{\frac{1}{2}}, \frac{1}{\frac{1}{2}} \right) = (2,2,2)$$

### 3. Face-center cubic



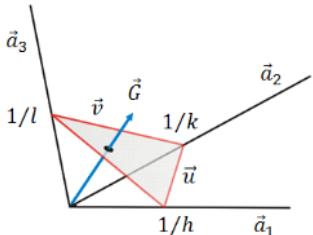
Intercepts:

$$n_1 = \frac{1}{2}, n_2 = \frac{1}{2}, n_3 = \infty$$

Reciprocals:

$$\left(\frac{1}{n_1}, \frac{1}{n_2}, \frac{1}{n_3}\right) = \left(\frac{1}{\frac{1}{2}}, \frac{1}{\frac{1}{2}}, \frac{1}{\infty}\right) = (2, 2, 0)$$

- (5) The orientation of a plane is determined by its normal vector. Suppose that the intercepts of a plane with primitive vectors of the real lattice are  $(1/h, 1/k, 1/l)$ .



Choose two vectors  $\vec{u}$  and  $\vec{v}$  lying on the real lattice plane.

$$\vec{u} = \frac{1}{k}\vec{a}_2 - \frac{1}{h}\vec{a}_1 \text{ and } \vec{v} = \frac{1}{k}\vec{a}_2 - \frac{1}{l}\vec{a}_3$$

$$\vec{G} \cdot \vec{u} = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot \left(\frac{1}{k}\vec{a}_2 - \frac{1}{h}\vec{a}_1\right) = 0$$

$$\vec{G} \cdot \vec{v} = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot \left(\frac{1}{k}\vec{a}_2 - \frac{1}{l}\vec{a}_3\right) = 0$$

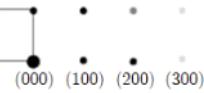
⇒ The reciprocal lattice vector  $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$  is perpendicular to the real lattice planes  $(hkl)$ .

⇒ Miller indices  $(hkl)$  are coordinates of the reciprocal lattice vector  $\vec{G}$  which is the orientation of a plane.

⇒ Each reciprocal lattice point defined by  $\vec{G}$  is associated with a family of planes of atoms.

## B. DIFFRACTION PATTERN AND STRUCTURE OF A UNIT CELL

- (1) The diffraction pattern of simple cubic for a zone axis of [100].



### diffraction pattern

From Bragg's law,  $2d \sin \theta = n\lambda$ , the spacing between the nearest planes can be found using the projection of  $\vec{a}_1$  on  $\frac{\vec{G}}{h}$ , i.e.,

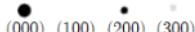
$$d_{hkl} = \frac{\vec{a}_1}{h} \cdot \frac{\vec{G}}{|\vec{G}|} = \frac{2\pi h}{h |\vec{G}|} = \frac{2\pi}{|\vec{G}|}$$

By convention, we set the diffraction order  $n = 1$  for XRD, i.e.,  $2d_{100} \sin \theta_1 = \lambda$

For  $n = 2$ , we just halve the  $d$ -spacing to make  $n = 1$ , i.e.,

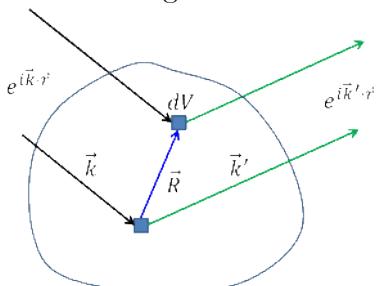
$$2d_{100} \sin \theta_2 = 2\lambda \Rightarrow 2 \frac{d_{100}}{2} \sin \theta_2 = \lambda \Rightarrow 2d_{200} \sin \theta_2 = \lambda$$

- (2) The diffraction pattern of body-center cubic for a zone axis of [100].



### diffraction pattern

Scattering occurs due to the interaction of the incident X-ray with the electron charge distributed in a solid with charge density  $n(\vec{r})$ .



The amplitude of scattering by an infinitesimal volume  $dV$  is

proportional to the charge at this point, i.e.,  $n(\vec{r})dV$ , and a phase factor  $e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}}$  acquired by the scattered waves.

The diffraction amplitude is given by

$$\begin{aligned} I &= \int n(\vec{r}) e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}} dV \\ &= \int n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} dV \\ &= \sum_R \int_{\text{cell}} n(\vec{r} + \vec{R}) e^{-i\vec{G} \cdot (\vec{r} + \vec{R})} dV \end{aligned}$$

Assume that the charge density is periodic, i.e.,  $n(\vec{r}) = n(\vec{r} + \vec{R})$

$$I = \sum_R e^{-i\vec{G} \cdot \vec{R}} \int_{\text{cell}} n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} dV = N_{\text{cell}} \int_{\text{cell}} n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} dV = N_{\text{cell}} S_G$$

where  $S_G$  is the structure factor

$$S_G = \int_{\text{cell}} n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} dV$$

- (3) It is convenient to write the charge density as the superposition of the charge densities associated with each atom of a unit cell.

$$\text{Let } n(\vec{r}) = \sum_i n_i(\vec{r} - \vec{r}_i)$$

$$S_G = \sum_i \int_{\text{cell}} n_i(\vec{r} - \vec{r}_i) e^{-i\vec{G} \cdot \vec{r}} dV$$

$$\text{Let } \vec{r} - \vec{r}_i = \vec{d}$$

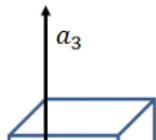
$$S_G = \sum_i e^{-i\vec{G} \cdot \vec{r}_i} \int_{\text{cell}} n_i(\vec{d}) e^{-i\vec{G} \cdot \vec{d}} dV = \sum_i e^{-i\vec{G} \cdot \vec{r}_i} f_i(\vec{G})$$

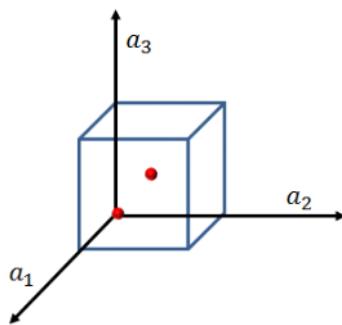
$$\text{where } f_i(\vec{G}) = \int_{\text{cell}} n_i(\vec{d}) e^{-i\vec{G} \cdot \vec{d}} dV$$

is the atomic form factor, which is determined by the charge density of atom  $i$  in a unit cell.

## EXAMPLES:

A bcc lattice contains two identical atoms





$$\vec{r}_1 = 0$$

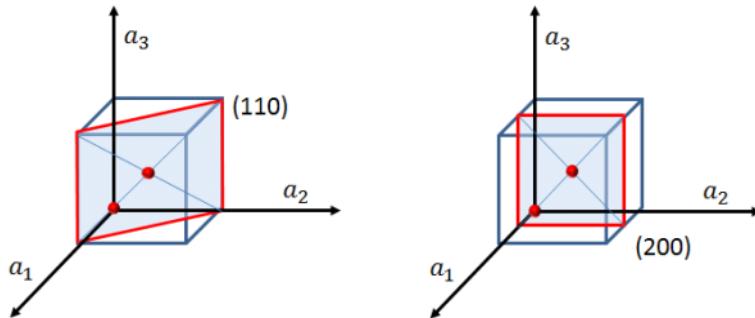
$$\vec{r}_2 = \frac{1}{2}(\vec{a}_1 + \vec{a}_2 + \vec{a}_3)$$

The atomic form factors are the same, i.e.,  $f_1 = f_2 = f$

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$\begin{aligned} S_G &= \sum_i f e^{-i\vec{G}\cdot\vec{r}_i} \\ &= f \left[ e^{-i0} + e^{-i\vec{G}\cdot(\vec{a}_1+\vec{a}_2+\vec{a}_3)/2} \right] \\ &= f [1 + e^{-i(h+k+l)\pi}] \\ &= f [1 + (-1)^{h+k+l}] \\ &= \begin{cases} 2f, & h+k+l = \text{even} \\ 0, & h+k+l = \text{odd} \end{cases} \end{aligned}$$

Diffraction peaks are observed, e.g., from (110), (200), (211) planes, but not from (100), (111), (210) planes.

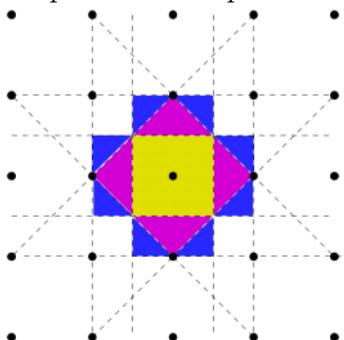


# 1-4 Brillouin Zone

Tuesday, May 14, 2013 4:08 PM

## A. FIRST BRILLOUIN ZONE (1930)

- (1) The Brillouin zone is defined by the area surrounded by the planes that are perpendicular bisectors of the vectors from the origin to the reciprocal lattice points.



The enclosed area is the first Brillouin zone (yellow area) when the vectors connect to the nearest neighbor points.

The enclosed area is the second Brillouin zone (pink area) when the vectors connect to the 2nd nearest neighbor points.

⋮

⇒ The first Brillouin zone is the Wigner-Seitz primitive cell in the reciprocal lattice.

- (2) The volume of the first Brillouin zone

$$\begin{aligned} V_{BZ} &= \left| \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \right| \\ &= \frac{2\pi}{V_{cell}} (\vec{a}_2 \times \vec{a}_3) \cdot \left[ \frac{2\pi}{V_{cell}} (\vec{a}_3 \times \vec{a}_1) \times \frac{2\pi}{V_{cell}} (\vec{a}_1 \times \vec{a}_2) \right] \\ &= \left( \frac{2\pi}{V_{cell}} \right)^3 \{ (\vec{a}_2 \times \vec{a}_3) \cdot [\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)] \vec{a}_1 - [\vec{a}_1 \cdot (\vec{a}_1 \times \vec{a}_2)] \vec{a}_3 \} \\ &= \left( \frac{2\pi}{V_{cell}} \right)^3 \{ (\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1 [\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)] \} \end{aligned}$$

Since  $V_{cell} = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)| = |\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)|$  = volume of a unit cell

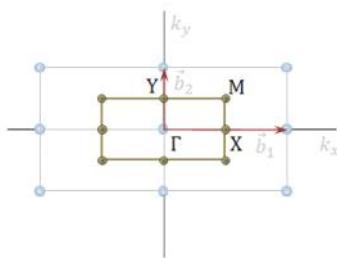
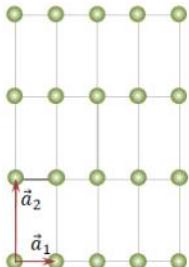
$$\mathcal{V}_{\text{BZ}} = \left( \frac{2\pi}{\mathcal{V}_{\text{cell}}} \right)^3 \mathcal{V}_{\text{cell}} \mathcal{V}_{\text{cell}} = \frac{(2\pi)^3}{\mathcal{V}_{\text{cell}}}$$

- (3) Zone boundary and symmetric points of the first Brillouin zone

  1. 2D rectangular lattice

## Real lattice

## Reciprocal lattice



Primitive vectors:

$$\begin{cases} \vec{a}_1 = (a_1, 0) \\ \vec{a}_2 = (0, a_2) \end{cases}, \quad \begin{cases} \vec{b}_1 = \left(\frac{2\pi}{a_1}, 0\right) \\ \vec{b}_2 = \left(0, \frac{2\pi}{a_2}\right) \end{cases}$$

Volume:

$$\mathcal{V}_{\text{cell}} = a_1 a_2, \quad \mathcal{V}_{\text{BZ}} = \frac{(2\pi)^2}{\mathcal{V}_{\text{cell}}} = \frac{(2\pi)^2}{a_1 a_2}$$

## Boundary:

$$k_x = \left[ -\frac{\pi}{a_1}, \frac{\pi}{a_1} \right], \quad k_y = \left[ -\frac{\pi}{a_2}, \frac{\pi}{a_2} \right]$$

Symmetric points:

$$\Gamma = (0,0)$$

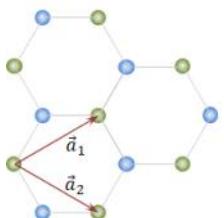
$$X = \left( \frac{\pi}{a_1}, 0 \right)$$

$$Y = \left(0, \frac{\pi}{a_2}\right)$$

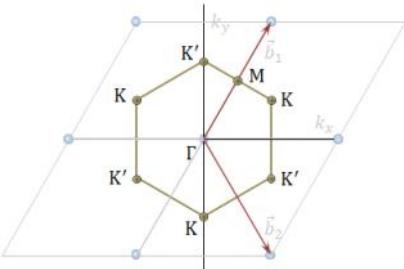
$$M = \left( \frac{\pi}{a_1}, \frac{\pi}{a_2} \right)$$

## 2. Honeycomb lattice

Real lattice



Reciprocal lattice



Primitive vectors:

$$\begin{cases} \vec{a}_1 = \frac{a}{2}(3, \sqrt{3}) \\ \vec{a}_2 = \frac{a}{2}(3, -\sqrt{3}) \end{cases}, \quad \begin{cases} \vec{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}) \\ \vec{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \end{cases}$$

Volume:

$$V_{\text{cell}} = \frac{3\sqrt{3}}{2}a^2, \quad V_{\text{BZ}} = \frac{(2\pi)^2}{V_{\text{cell}}} = \frac{2(2\pi)^2}{3\sqrt{3}a^2}$$

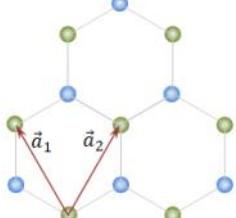
Symmetric points:

$$K = \left(\frac{4\pi}{3a}, 0\right)$$

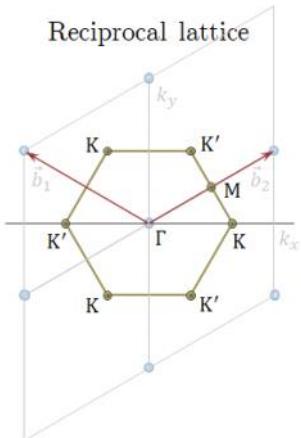
$$K' = \left(\frac{\pi}{\sqrt{3}a}, \frac{\pi}{a}\right)$$

$$M = \left(\frac{\pi}{a}, \frac{\pi}{\sqrt{3}a}\right)$$

Real lattice



Reciprocal lattice



Primitive vectors:

$$\vec{a}_1 = \frac{a}{2}(\sqrt{3}, 3), \quad \vec{a}_2 = \frac{a}{2}(-\sqrt{3}, 3)$$

$$\vec{b}_1 = \frac{2\pi}{3a}(\sqrt{3}, 1), \quad \vec{b}_2 = \frac{2\pi}{3a}(-\sqrt{3}, 1)$$

Symmetric points:

$$K = \left( \frac{\pi}{a}, \frac{\pi}{\sqrt{3}a} \right)$$

$$K' = \left( 0, \frac{4\pi}{3a} \right)$$

$$M = \left( \frac{\pi}{\sqrt{3}a}, \frac{\pi}{a} \right)$$

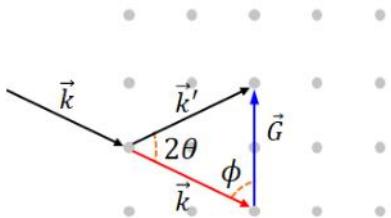
## B. PHYSICAL INTERPRETATION OF ZONE BOUNDARY

- (1) From Laue's diffraction condition

$$\vec{k}' - \vec{k} = \vec{G}$$

As the scattering is elastic, i.e.,  $|\vec{k}| = |\vec{k}'|$

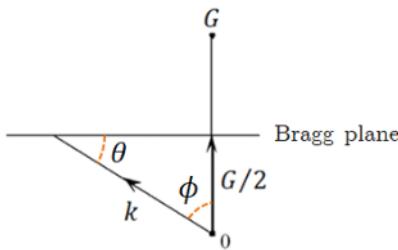
Reciprocal lattice



$$\vec{k}' = \vec{k} + \vec{G} \Rightarrow |\vec{k}'|^2 = |\vec{k} + \vec{G}|^2 = |\vec{G}|^2 + 2\vec{k} \cdot \vec{G} + |\vec{k}|^2 \Rightarrow 0 = |\vec{G}|^2 + 2\vec{k} \cdot \vec{G}$$

Replacing  $\vec{G}$  to  $-\vec{G}$ , which also satisfy the translational symmetry of the reciprocal lattice. We obtain

$$2\vec{k} \cdot \vec{G} = |\vec{G}|^2 \Rightarrow \vec{k} \cdot \frac{\vec{G}}{|\vec{G}|} = \frac{|\vec{G}|}{2} \Rightarrow \vec{k} \cdot \hat{G} = \frac{|\vec{G}|}{2}$$



$$\vec{k} \cdot \hat{G} = k \cos \phi = k \cos \left( \frac{\pi}{2} - \theta \right) = k \sin \theta = \frac{|\vec{G}|}{2}$$

$\Rightarrow$  The vector  $\vec{k}$  lies on the Bragg plane satisfied the diffraction condition.

### EXAMPLES:

- Find the planes which are responsible for each Bragg peak by assigning the correct  $hkl$

$$k \sin \theta = \frac{|\vec{G}|}{2} \Rightarrow \frac{2\pi}{\lambda} \sin \theta = \frac{1}{2} \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}$$

$$\Rightarrow \sin \theta = \frac{\lambda}{2a} \sqrt{h^2 + k^2 + l^2}$$

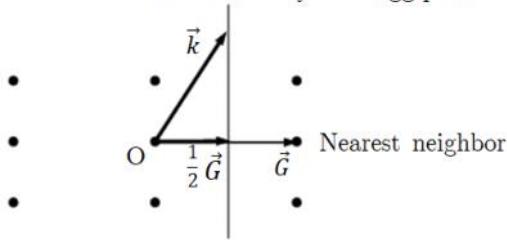
For a simple cubic, all integral values of  $hkl$  are possible

$hkl$	$h^2 + k^2 + l^2$
100	1
110	2
111	3
200	4
210	5
211	6
220	8
300, 221	9

The value 7 is missing in the sequence, since there is no possible integral value that  $h^2 + k^2 + l^2 = 7$ .

- The Bragg plane is equivalent to the zone boundary of the first Brillouin zone.

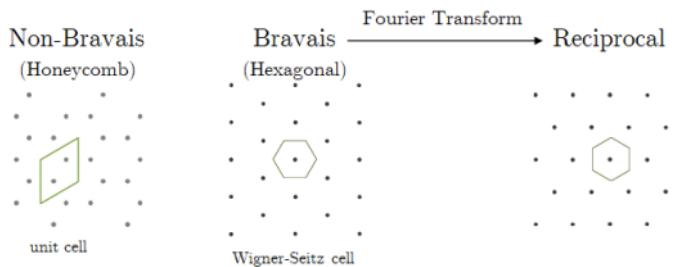
Zone boundary = Bragg plane



⇒ The vector  $\vec{k}$  at the zone boundary satisfies the diffraction condition.

### (3) Unit cell and first Brillouin zone

Real Lattice



Miller index ←———— Diffraction pattern



## 2-1 Bloch Theorem

Tuesday, December 20, 2011 8:30 PM

### A. SCHRÖDINGER EQUATION ON RECIPROCAL LATTICE

- (1) The Schrödinger equation of an electron on a lattice

$$\hat{\mathcal{H}}\psi(\vec{r}) = \left[ \frac{\hat{p}^2}{2m} + V(\vec{r}) \right] \psi(\vec{r}) = \left[ \frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = \varepsilon \psi(\vec{r})$$

where  $\psi(\vec{r})$  are eigenfunctions and  $\varepsilon$  are eigenenergies.

For periodic potentials,  $V(\vec{r} + \vec{R}) = V(\vec{r})$ , where  $\vec{R}$  is the translation vector on the direct lattice,  $V(\vec{r})$  can be expanded in a Fourier series of the reciprocal lattice vector  $\vec{G}$ ,

$$V(\vec{r}) = \sum_G V_G e^{i\vec{G}\cdot\vec{r}}$$

- (2) Assume that the eigenfunctions of the Hamiltonian can be expanded in terms of the plane waves, as follows,

$$\psi(\vec{r}) = \sum_k c_k e^{i\vec{k}\cdot\vec{r}}, \text{ where } \vec{k} \in \vec{k}\text{-space}$$

The Schrödinger equations become

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_G V_G e^{i\vec{G}\cdot\vec{r}} \right] \sum_k c_k e^{i\vec{k}\cdot\vec{r}} = \varepsilon \sum_k c_k e^{i\vec{k}\cdot\vec{r}}$$

$$\sum_k \frac{\hbar^2 k^2}{2m} c_k e^{i\vec{k}\cdot\vec{r}} + \sum_{G,k} V_G c_k e^{i(\vec{G}+\vec{k})\cdot\vec{r}} = \varepsilon \sum_k c_k e^{i\vec{k}\cdot\vec{r}}$$

$$\sum_k \left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k e^{i\vec{k}\cdot\vec{r}} + \sum_{G,k'} V_G c_{k'-G} e^{i\vec{k}'\cdot\vec{r}} = 0$$

Relabel  $k' \rightarrow k$  and  $G \rightarrow G'$

$$\sum_k \left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k e^{i\vec{k}\cdot\vec{r}} + \sum_{k,G'} V_{G'} c_{k-G'} e^{i\vec{k}\cdot\vec{r}} = 0$$

$$\sum_k e^{i\vec{k}\cdot\vec{r}} \left[ \left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k + \sum_{G'} V_{G'} c_{k-G'} \right] = 0$$

$$\Rightarrow \left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k + \sum_{G'} V_{G'} c_{k-G'} = 0$$

(3) Solutions of the central equation

Let  $\vec{k} \rightarrow \vec{k} - \vec{G}$  (since  $\vec{G}$  is a translational vector in a reciprocal lattice)

$$\left[ \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m} - \varepsilon \right] c_{k-G} + \sum_{G'} V_{G'} c_{k-G-G'} = 0$$

Let  $\vec{G}' \rightarrow \vec{G}' - \vec{G}$

$$\left[ \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m} - \varepsilon \right] c_{k-G} + \sum_{G'} V_{G'-G} c_{k-G'} = 0 \dots \text{(Central Equation)}$$

$$\begin{pmatrix} \frac{\hbar^2 (\vec{k} - \vec{G}_1)^2}{2m} - \varepsilon & V_{G_2-G_1} & \dots \\ V_{G_1-G_2} & \frac{\hbar^2 (\vec{k} - \vec{G}_2)^2}{2m} - \varepsilon & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{k-G_1} \\ c_{k-G_2} \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \end{pmatrix}$$

$$\begin{pmatrix} \frac{\hbar^2 (\vec{k} - \vec{G}_1)^2}{2m} & V_{G_2-G_1} & \dots \\ V_{G_1-G_2} & \frac{\hbar^2 (\vec{k} - \vec{G}_2)^2}{2m} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{k-G_1} \\ c_{k-G_2} \\ \vdots \end{pmatrix} = \varepsilon \begin{pmatrix} c_{k-G_1} \\ c_{k-G_2} \\ \vdots \end{pmatrix}$$

For a given  $\vec{k}$ , the eigenvalues are the corresponding energies, i.e.,  $\varepsilon \rightarrow \varepsilon_k$ .

## B. BLOCH [B-loch] WAVEFUNCTION

(1) For a translational system in a reciprocal lattice, a given  $\vec{k}$  can be replaced by  $\vec{k} - \vec{G}$ . Therefore  $\vec{k}$  in the eigenfunction can be considered to restrict in the first Brillouin zone, as

$$\psi(\vec{r}) = \sum_k c_k e^{i\vec{k}\cdot\vec{r}} = \sum_{k \in BZ} \sum_G c_{k-G} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} = \sum_{k \in BZ} e^{i\vec{k}\cdot\vec{r}} \sum_G c_{k-G} e^{-i\vec{G}\cdot\vec{r}}$$

where  $c_{k-G}$  are solutions of the central equation.

$$\text{Let } u_k(\vec{r}) = \sum_G c_{k-G} e^{-i\vec{G}\cdot\vec{r}}$$

$$\Rightarrow \psi(\vec{r}) = \sum_{\vec{k} \in \text{BZ}} u_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

Let  $\psi_k(\vec{r}) = \boxed{u_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}}}$  .....Bloch wavefunction for a given value of  $\vec{k}$ .

- (2) Translation of the Bloch wavefunctions  $\psi_k(\vec{r})$

In direct lattice:

$$\psi_k(\vec{r} + \vec{R}) = u_k(\vec{r} + \vec{R}) e^{i\vec{k}\cdot(\vec{r} + \vec{R})}$$

Here,

$$u_k(\vec{r} + \vec{R}) = \sum_G c_{k-G} e^{-i\vec{G}\cdot(\vec{r} + \vec{R})} = e^{-i\vec{G}\cdot\vec{R}} \sum_G c_{k-G} e^{-i\vec{G}\cdot\vec{r}} = u_k(\vec{r})$$

$\Rightarrow u_k(\vec{r})$  is a periodic function with period  $\vec{R}$ , i.e.,

$$\boxed{u_k(\vec{r} + \vec{R}) = u_k(\vec{r})}$$

Therefore,

$$\psi_k(\vec{r} + \vec{R}) = u_k(\vec{r}) e^{i\vec{k}\cdot(\vec{r} + \vec{R})} = u_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{R}} = \psi_k(\vec{r}) e^{i\vec{k}\cdot\vec{R}}$$

$\Rightarrow$  Covariance of the wavefunction with respect to the translational symmetry in the real space.

In reciprocal lattice:

$$\psi_{k+G}(\vec{r}) = u_{k+G}(\vec{r}) e^{i(\vec{k} + \vec{G})\cdot\vec{r}} = \sum_{G'} c_{k+G-G'} e^{-i\vec{G}'\cdot\vec{r}} e^{i(\vec{k} + \vec{G})\cdot\vec{r}}$$

Let  $\vec{G}' - \vec{G} \rightarrow \vec{G}'$

$$\psi_{k+G}(\vec{r}) = \sum_{G'} c_{k-G'} e^{-i\vec{G}'\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}} = u_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}} = \psi_k(\vec{r})$$

$\Rightarrow$  The Bloch wavefunction  $\psi_k$  is periodic in the reciprocal space, i.e.,  $\boxed{\psi_{k+G} = \psi_k}$

## 2-2 Crystal Momentum and Band

Tuesday, December 20, 2011 8:30 PM

### A. CRYSTAL MOMENTUM $\vec{k}$

- (1) The Schrödinger equation with a Bloch wavefunction is

$$\begin{aligned}\hat{\mathcal{H}}\psi_k(\vec{r}) &= \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \\ &= -\frac{\hbar^2}{2m} \nabla \left( i\vec{k} u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} + \nabla u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \right) + V(\vec{r}) u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \\ &= e^{i\vec{k} \cdot \vec{r}} \left[ -\frac{\hbar^2}{2m} \left( -k^2 + 2i\vec{k} \cdot \nabla + \nabla^2 \right) + V(\vec{r}) \right] u_k(\vec{r}) \\ &= e^{i\vec{k} \cdot \vec{r}} \left[ \frac{\hbar^2}{2m} \left( -i\nabla + \vec{k} \right)^2 + V(\vec{r}) \right] u_k(\vec{r})\end{aligned}$$

For a given value of  $\vec{k}$ , let

$$\hat{\mathcal{H}}_k = \frac{\hbar^2}{2m} \left( -i\nabla + \vec{k} \right)^2 + V(\vec{r}) = \frac{(\hat{\mathbf{p}} + \hbar\vec{k})^2}{2m} + V(\vec{r})$$

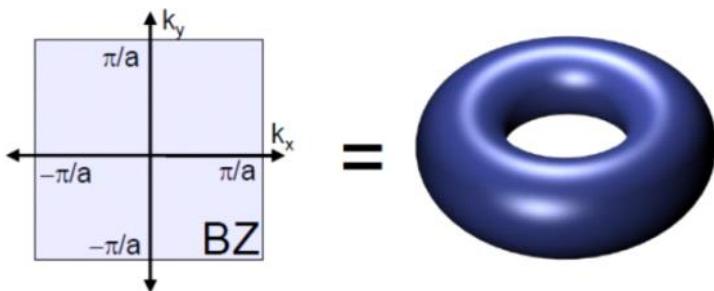
Here,  $\hat{\mathbf{p}} = -i\hbar\nabla$  is the momentum operator and  $\hbar\vec{k}$  is called crystal momentum associated with electrons in a crystal lattice.

$$\Rightarrow \hat{\mathcal{H}}\psi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \hat{\mathcal{H}}_k u_k(\vec{r})$$

- (2) Since  $\psi_{k+G}(\vec{r}) = \psi_k(\vec{r})$

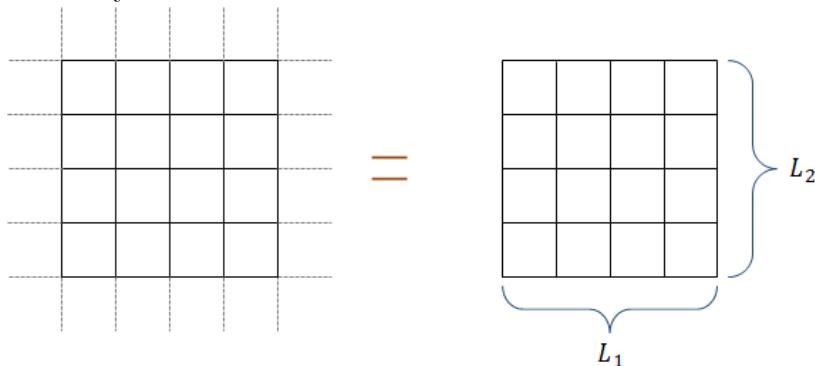
The crystal momentum  $\vec{k}$  is conserved to within a reciprocal lattice vector  $\vec{G}$ , i.e.,  $\vec{k} \sim \vec{k} \bmod \vec{G}$ .

$\Rightarrow$  The wave vector  $\vec{k}$  lives on a torus



(3) Number of crystal momentum:

An infinite lattice can be approximated by a finite lattice with periodic boundary conditions.



Apply the periodic boundary conditions (Born-von Karman)

$$\psi_k(\vec{r} + \vec{L}) = \psi_k(\vec{r})$$

where  $L_1 = N_1 a_1$ ,  $L_2 = N_2 a_2$ ,  $L_3 = N_3 a_3$ , and  $N_1, N_2, N_3$  are the total number of primitive cells along the  $i$ -th axis in the crystal.

Use the Bloch theorem

$$\psi_k(r_i + N_i a_i) = \psi_k(r_i) e^{ik_i N_i a_i} = \psi_k(r_i)$$

$$\Rightarrow e^{ik_i N_i a_i} = 1$$

$$\Rightarrow k_i N_i a_i = 2\pi \ell_i$$

$$\Rightarrow k_i = \frac{2\pi \ell_i}{N_i a_i} \text{ where } \ell_i \text{ is integer}$$

Suppose that  $k_i$  is restricted to the first Brillouin zone, i.e.,

$$-\frac{\pi}{a_i} \leq k_i < \frac{\pi}{a_i} \Rightarrow -\frac{\pi}{a_i} \leq \frac{2\pi \ell_i}{N_i a_i} < \frac{\pi}{a_i} \Rightarrow -\frac{N_i}{2} \leq \ell_i < \frac{N_i}{2}$$

$\Rightarrow$  The number of allowed  $k$ -values in the first Brillouin zone is equal to the number of unit cells in the crystal.

$$\text{Since } \Delta k_i = \frac{2\pi}{N_i a_i} = \frac{2\pi}{L_i}$$

$\Rightarrow \vec{k}$  is discretized. When  $\mathcal{V}$  is taken to infinity (thermodynamic limit),  $\Delta k \rightarrow 0$ , the  $\vec{k}$  values tend to a continuum.

## C. BAND $n$

(1) For each translation vector  $\vec{R}$  of the Bravais lattice, we define a lattice

translation operator  $\hat{T}_R$  by

$$\hat{T}_R \psi_k(\vec{r}) = \psi_k(\vec{r} + \vec{R})$$

Thus, we can obtain

$$\begin{aligned} [\hat{T}_R, \hat{\mathcal{H}}] \psi_k(\vec{r}) &= \hat{T}_R \hat{\mathcal{H}}(\vec{r}) \psi_k(\vec{r}) - \hat{\mathcal{H}}(\vec{r}) \hat{T}_R \psi_k(\vec{r}) \\ &= \hat{\mathcal{H}}(\vec{r} + \vec{R}) \psi_k(\vec{r} + \vec{R}) - \hat{\mathcal{H}}(\vec{r}) \psi_k(\vec{r} + \vec{R}) \\ &= \hat{\mathcal{H}}(\vec{r}) \psi_k(\vec{r} + \vec{R}) - \hat{\mathcal{H}}(\vec{r}) \psi_k(\vec{r} + \vec{R}) \\ &= 0 \end{aligned}$$

$\Rightarrow \psi_k(\vec{r})$  is the common eigenfunction of  $\hat{T}_R$  and  $\hat{\mathcal{H}}$ .

$$\Rightarrow \begin{cases} \hat{\mathcal{H}} \psi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \hat{\mathcal{H}}_k u_k(\vec{r}) = \lambda \psi_k(\vec{r}) \\ \hat{T}_R \psi_k(\vec{r}) = \psi_k(\vec{r} + \vec{R}) = \alpha \psi_k(\vec{r}) \end{cases}$$

According to the Bloch theorem  $\psi_k(\vec{r} + \vec{R}) = \psi_k(\vec{r}) e^{i\vec{k} \cdot \vec{R}}$

$\Rightarrow \alpha = e^{i\vec{k} \cdot \vec{R}}$  the eigenvalue of  $\hat{T}_R$ .

Let  $\hat{\mathcal{H}}_{\vec{k}} u_k(\vec{r}) = \varepsilon_k u_k(\vec{r})$

$$\Rightarrow \hat{\mathcal{H}} \psi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \hat{\mathcal{H}}_k u_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \varepsilon_k u_k(\vec{r}) = \varepsilon_k \psi_k(\vec{r})$$

$\Rightarrow \lambda = \varepsilon_k$  the eigenvalue of  $\hat{\mathcal{H}}$ .

Since

$$\begin{aligned} \hat{\mathcal{H}} \psi_{k+G}(\vec{r}) &= \varepsilon_{k+G} \psi_{k+G}(\vec{r}) \text{ and } \psi_{k+G}(\vec{r}) = \psi_k(\vec{r}) \\ \Rightarrow \hat{\mathcal{H}} \psi_k(\vec{r}) &= \varepsilon_{k+G} \psi_k(\vec{r}) \end{aligned}$$

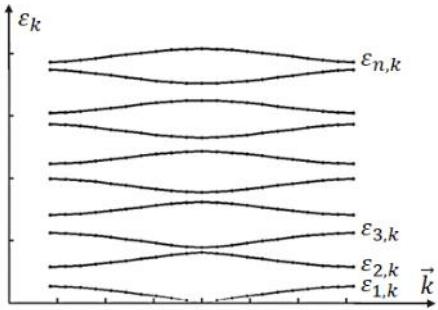
$\Rightarrow$  The eigenvalues do not change when  $\vec{k}$  is replaced by  $\vec{k} + \vec{G}$  (consequence of the conservation of crystal momentum).

$\Rightarrow$  The eigenenergy  $\varepsilon_k$  is periodic in  $\vec{k}$ -space, i.e.,  $\boxed{\varepsilon_{k+G} = \varepsilon_k}$

- (2) According to Sturm-Liouville theory, there are infinite discrete eigenvalues which can be labelled by  $n$ , i.e., in  $\vec{k}$ -space, each value of  $\vec{k}$  corresponding to infinite eigenvalues.

$$\hat{\mathcal{H}} \psi_{nk}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \hat{\mathcal{H}}_k u_{nk}(\vec{r}) = \varepsilon_{nk} \psi_{nk}(\vec{r})$$

These eigenvalues are called "energy band" and noted as  $\varepsilon_{nk} \equiv \varepsilon_n(\vec{k})$ .



- (3) For a given  $\vec{k}$  value, a Bloch factor  $u_{nk}(\vec{r})$  satisfies the eigenvalue equation:

$$\hat{\mathcal{H}}_k u_{nk}(\vec{r}) = \varepsilon_{nk} u_{nk}(\vec{r})$$

subject to a periodic boundary condition over a unit cell.

OS:

Since Bloch states corresponding to different crystal momentum (Bloch wavevectors  $\vec{k}$ ) constitute separate eigensystems, it is meaningless to consider an orthonormality relation between Bloch factors unless they have the same  $\vec{k}$ .

Thus, we obtain a relation for the orthogonality of Bloch factors  $u_{nk}(\vec{r})$  with respect to the band index  $n$ :

$$\frac{1}{\mathcal{V}_{\text{cell}}} \int_{\text{cell}} u_{nk}^*(\vec{r}) u_{n'k'}(\vec{r}) d^3r = \delta_{n,n'}$$

Therefore,

$$\begin{aligned} \int \psi_{nk}^*(\vec{r}) \psi_{n'k'}(\vec{r}) d^3r &= \frac{1}{\mathcal{V}} \sum_R \int_{\text{unit cell}} \psi_{nk}^*(\vec{r} + \vec{R}) \psi_{n'k'}(\vec{r} + \vec{R}) d^3r \\ &= \frac{1}{\mathcal{V}} \sum_R e^{-i(\vec{k}-\vec{k}') \cdot \vec{R}} \\ &\quad \times \int u_{nk}^*(\vec{r} + \vec{R}) e^{-i\vec{k} \cdot \vec{r}} u_{n'k'}(\vec{r} + \vec{R}) e^{i\vec{k}' \cdot \vec{r}} d^3r \end{aligned}$$

Since  $\mathcal{V} = N_{\text{cell}} \mathcal{V}_{\text{cell}}$

$$\begin{aligned}
\int \psi_{nk}^*(\vec{r}) \psi_{n'k'}(\vec{r}) d^3r &= \frac{1}{N_{\text{cell}}} \sum_R e^{-i(\vec{k}-\vec{k}') \cdot \vec{R}} \\
&\quad \times \frac{1}{V_{\text{cell}}} \int_{\text{cell}} u_{nk}^*(\vec{r}) u_{n'k}(\vec{r}) e^{-i(\vec{k}-\vec{k}') \cdot \vec{r}} d^3r \\
&= \delta_{k,k'} \frac{1}{V_{\text{cell}}} \int_{\text{cell}} u_{nk}^*(\vec{r}) u_{n'k}(\vec{r}) d^3r \\
&= \delta_{k,k'} \delta_{n,n'}
\end{aligned}$$

⇒ Bloch states are orthonormal.

Considering

$$\begin{aligned}
\sum_n \sum_{k \in \text{BZ}} \psi_{nk}^*(\vec{r}) \psi_{nk}(\vec{r}') &= \sum_n \sum_{k \in \text{BZ}} u_{nk}^*(\vec{r}) u_{nk}(\vec{r}') e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \\
&= \sum_{k \in \text{BZ}} e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} = \delta(\vec{r} - \vec{r}'')
\end{aligned}$$

⇒ Bloch states are completeness.

⇒ Bloch states form a set of basis.

## 2-3 Supercells

Tuesday, December 20, 2011 8:30 PM

### A. INTRINSICALLY APERIODIC SYSTEMS

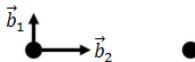
#### (1) Modulated crystallography

##### 1. Periodic crystal



The XRD pattern is the reciprocal lattice points.

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$



##### 2. Commensurately modulated aperiodic crystal

A supercell is constructed by an integral number of unit cells larger than the original unit cell.



The new periodicity with a characteristic wavevector  $\vec{q}$  is a rational fraction or multiple of the lattice constant. The XRD pattern is modulated and the standard periodic main reflections are surrounded by satellite reflections.

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 + m\vec{q}$$

The satellite locations are defined by a  $\vec{q}$  vector

$$\vec{q} = q_1\vec{b}_1 + q_2\vec{b}_2 + q_3\vec{b}_3$$

All components of the  $\vec{q}$  vector are rational.



$$\vec{b}_1$$



$$\vec{q} = 0.25\vec{b}_1$$

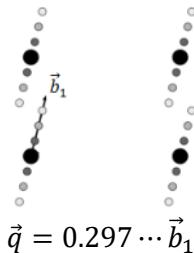
##### 3. Incommensurately modulated aperiodic crystal

A structure can NOT repeat on a unit-cell boundary.



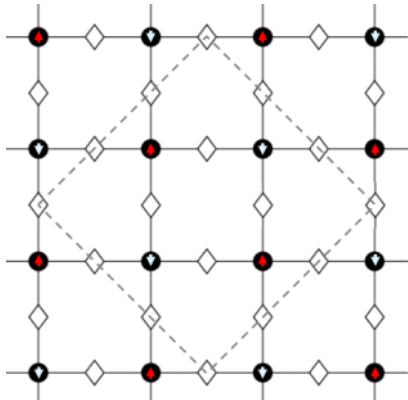
The new periodicity is irrational.

The XRD pattern shows satellite peaks of  $\vec{q}$  vector, at least one component is irrational.

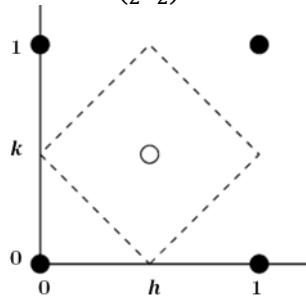


### EXAMPLES:

1. Structure of CuO plane and antiferromagnetic order.

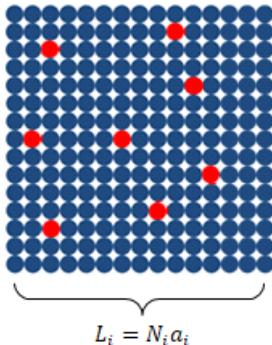


The solid line indicates the chemical unit cell, while the dashed line indicates the doubled area of the antiferromagnetic unit cell. Reciprocal space showing fundamental Bragg peak (filled circle) positions and antiferromagnetic superlattice peak (open circle) at  $(h, k) = \left(\frac{1}{2}, \frac{1}{2}\right)$ .



### (2) Defects

Suppose that the interaction between the impurities can be ignored.

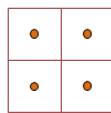


## B. SUPERCELLS

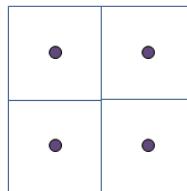
- (1) Take a large enough size of lattices as a unit cell, called supercell. The infinite periodic lattice is modeled by a large number of supercells stacked together through periodic boundary conditions.
- (2) Supercell in reciprocal space

Unit cell:

Real space



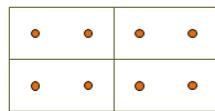
Reciprocal space



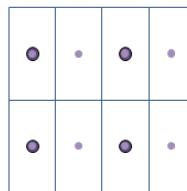
$$\vec{G} = \frac{2\pi}{a_1} \text{ (dark purple)}$$

Supercell:

Real space



Reciprocal space



$$\vec{K} = \frac{2\pi}{a'_1} = \frac{2\pi}{2a_1} = \frac{1}{2}\vec{G} \text{ (small light purple)}$$

The larger BZ of the unit cell can be reproduced by repeating the smaller BZ of the supercell using the reciprocal vectors.

- (3) Since the potential is periodic in the unit cell, the Fourier transform of the potential  $V(\vec{r})$  must be zero on all extra grid points (small light purple) in the reciprocal space of the unit cell, i.e.,

$$V(\vec{r}) = \sum_G V_G e^{i\vec{G}\cdot\vec{r}}$$

The Bloch wavefunctions  $\psi_k(\vec{r}) = u_k(\vec{r})e^{i\vec{k}\cdot\vec{r}}$  are not necessarily periodic in the unit cell, and therefore are not zero on the extra grid points (small light purple) in the reciprocal space of the unit cell. The Bloch wavefunctions  $\psi_k(\vec{r})$  on  $\vec{k} = 0$  (dark purple) and  $\vec{k} = \frac{1}{2}\vec{G}$  (small light purple) will behave independently.

$\Rightarrow$  There is no term in the Hamiltonian which can take a component of  $\psi_k(\vec{r})$  on  $\vec{k} = 0$  (dark purple) and create one on  $\vec{k} = \frac{1}{2}\vec{G}$  (small light purple). So one can solve for these points as two distinct sets.

- (4) Let  $L_i = N_i a_i$  be the length of a supercell and  $M_i L_i$  be the size of a crystal.

Apply the periodic boundary conditions

$$\psi_k(\vec{r} + M\vec{L}) = \psi_k(\vec{r})e^{i\vec{k}\cdot M\vec{L}} = \psi_k(\vec{r})$$

$$\Rightarrow e^{i\sum_i k_i M_i N_i a_i} = 1 \text{ where } i = x, y, z$$

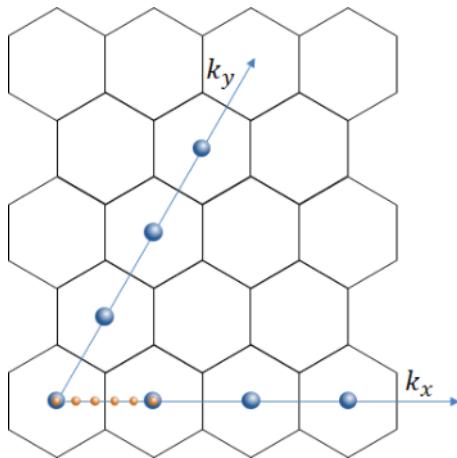
$$\Rightarrow k_i M_i N_i a_i = 2\pi\ell_i \text{ where } \ell_i = 0, \dots, M_i N_i - 1$$

$$\Rightarrow k_i = \frac{2\pi\ell_i}{M_i N_i a_i} = \frac{\ell_i}{M_i} K_i = \frac{\ell_i}{M_i N_i} G_i$$

The Bloch wavefunctions for each supercell are

$$\psi_k(\vec{r}) = u_k(\vec{r})e^{i\sum_i \frac{\ell_i}{M_i N_i} G_i r_i}$$

EXAMPLES:



Blue dot: reciprocal lattice sites of a unit cell, e.g.,  $1 \times 40$

Orange dot: reciprocal lattice sites of a supercell, e.g., 5

The Bloch wavefunctions for each supercell, i.e.,  $\ell = 0, \dots, 4$ , are

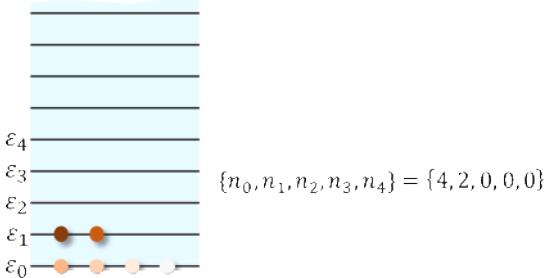
$$\psi_k(\vec{r}) = u_k(\vec{r}) e^{i \frac{\ell}{5 \times 40} \vec{G} \cdot \vec{r}} \text{ where } \vec{G} = \left( \frac{2\pi}{\sqrt{3}a}, 0 \right)$$

# 3-1 Review of Statistical Physics

Tuesday, December 20, 2011 8:29 PM

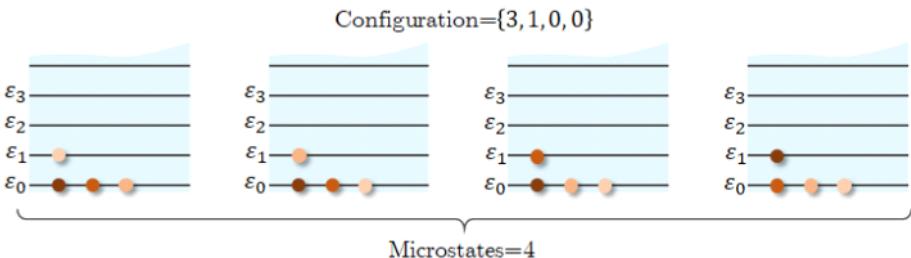
## A. MICROSTATES (Boltzmann, 1868)

- (1) We consider a system composed of  $N$  particles. Any individual particles may exist in states with energies  $\varepsilon_0, \varepsilon_1, \dots, \varepsilon_k$ . At any instant there will be  $n_0$  particles in the state with energy  $\varepsilon_0$ ,  $n_1$  with  $\varepsilon_1$ , and so on.



The specification of the set of populations  $n_0, n_1, \dots, n_k$  in the form  $\{n_0, n_1, \dots, n_k\}$  is a statement of the instantaneous configuration of the system.

- (2) A configuration  $\{n_0, n_1, n_2, \dots, n_k\}$  can be achieved in  $W$  different ways, where  $W$  is called the **microstates** of the configuration.



The microstates of the configuration  $\{n_0, n_1, n_2, \dots, n_k\}$  is given by the expression

$$\begin{aligned}
W &= C_{n_0}^N \times C_{n_1}^{N-n_0} \times C_{n_2}^{N-n_0-n_1} \times \dots \\
&= \frac{N!}{n_0!(N-n_0)!} \times \frac{(N-n_0)!}{n_1!(N-n_0-n_1)!} \times \frac{(N-n_0-n_1)!}{n_2!(N-n_0-n_1-n_2)!} \times \dots \\
&= \frac{N!}{n_0! n_1! n_2! \dots} \\
&= \prod_{i=0}^k \frac{N!}{n_i!}
\end{aligned}$$

where  $N = n_0 + n_1 + n_2 + \dots$

The total microstates are  $W_{\text{tot}} = k^N$

### EXAMPLES:

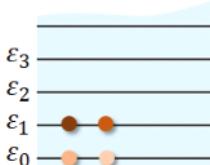
- Consider a system composed of 4 particles and 4 energy levels  $\varepsilon_0$ ,  $\varepsilon_1$ ,  $\varepsilon_2$ , and  $\varepsilon_3$ , where

$$\varepsilon_1 = 2\varepsilon_0$$

$$\varepsilon_2 = 3\varepsilon_0$$

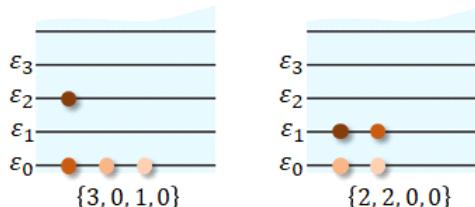
$$\varepsilon_3 = 4\varepsilon_0$$

- The microstates of the configuration  $\{2, 2, 0, 0\}$  are



$$W = C_2^4 \times C_2^2 \times C_0^0 \times C_0^0 = \frac{4!}{2! 2! 0! 0!} = 6$$

- The microstates of the energy  $E = 6\varepsilon_0$



The microstates of the configuration  $\{3, 0, 1, 0\}$  are

$$W = C_3^4 \times C_0^0 \times C_1^1 \times C_0^0 = \frac{4!}{3! 0! 1! 0!} = 4$$

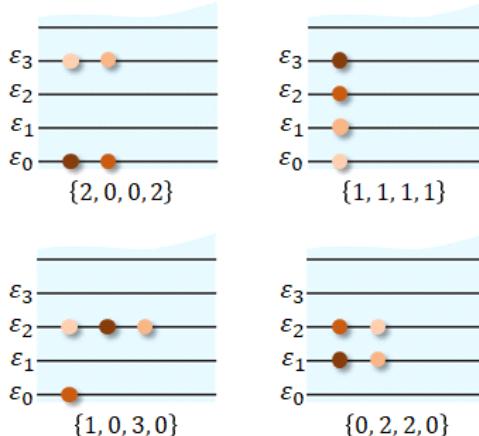
The microstates of the configuration  $\{2, 2, 0, 0\}$  are

$$W = C_2^4 \times C_2^2 \times C_0^0 \times C_0^0 = \frac{4!}{2! 2! 0! 0!} = 6$$

The microstates of the energy are  $W(E) = W(6\varepsilon_0) = 10$

(c) The microstates of the average energy

$$\bar{E} = \frac{4\epsilon_0 + 16\epsilon_0}{2} = 10\epsilon_0$$



The microstates of the configuration  $\{2, 0, 0, 2\}$  are

$$W = C_2^4 \times C_0^0 \times C_0^0 \times C_2^2 = \frac{4!}{2! 0! 0! 2!} = 6$$

The microstates of the configuration  $\{1, 1, 1, 1\}$  are

$$W = C_1^4 \times C_1^3 \times C_1^2 \times C_1^1 = \frac{4!}{1! 1! 1! 1!} = 24$$

The microstates of the configuration  $\{1, 0, 3, 0\}$  are

$$W = C_1^4 \times C_0^0 \times C_3^3 \times C_0^0 = \frac{4!}{1! 0! 3! 0!} = 4$$

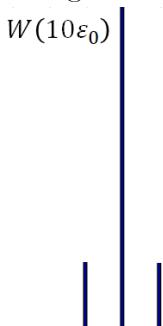
The microstates of the configuration  $\{0, 2, 2, 0\}$  are

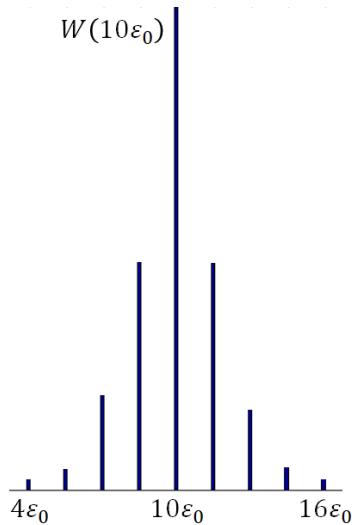
$$W = C_0^0 \times C_2^4 \times C_2^2 \times C_0^0 = \frac{4!}{0! 2! 2! 0!} = 6$$

The microstates of the average energy are  $W(\bar{E}) =$

$$W(10\epsilon_0) = 40$$

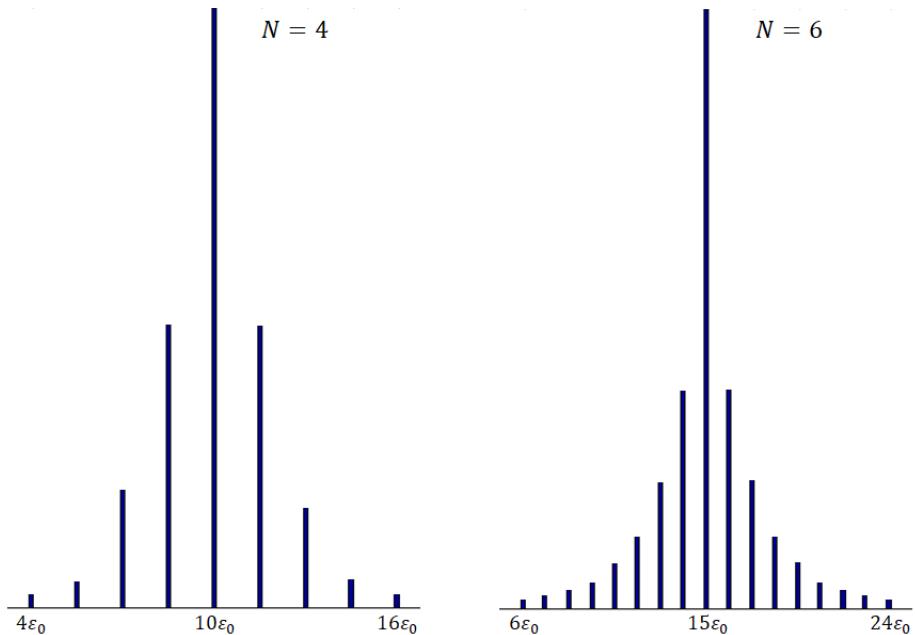
The histogram of the microstates as a function of the energy  $E$





The configurations of  $\bar{E} = 10\epsilon_0$  have greatest microstates.

- (3) According to the Central Limit Theorem, the microstates of the energy are



The configurations of the average energy  $\bar{E}$  have the greatest microstates and dominates all the rest, as  $N$  becomes larger.

- (4) The dominating configuration can be found by looking for the values of  $n_i$  that lead to a maximum value of  $W$ .

For a typical system,  $N$  is big and  $W$  is enormous. It turns out to be more convenient to deal with the natural logarithm of the microstates,  $\ln W$ , rather than with the weight itself, i.e.,

$$\ln W = \ln \left( \prod_{i=0}^k \frac{N!}{n_i!} \right) = \ln N! - \sum_i \ln n_i!$$

For large  $N$ , the Stirling's approximation gives

$$\ln N! \approx N \ln N - N$$

$$\ln n_i! \approx n_i \ln n_i - n_i$$

$$\Rightarrow \ln W \approx N \ln N - N - \sum_i (n_i \ln n_i - n_i) = N \ln N - \sum_i n_i \ln n_i$$

## B. ENSEMBLE (Gibbs, 1878)

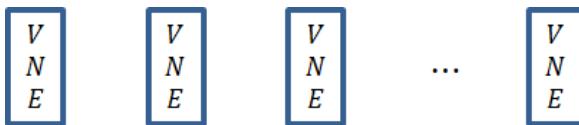
OS:

Introduction to Statistical Mechanics by Peter Eastman

<https://web.stanford.edu/~peastman/statmech/index.html>

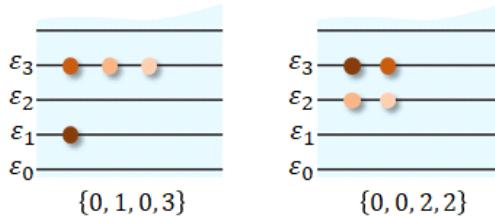
- (1) The macroscopic observables are average over a collection of the huge number of microstates under external constraints.
- (2) In statistics, macrostates are averages computed using **time averages** where the probability of the system being in a microstate as the fraction of time it spends in that state.  
However, in practice we have only one system in one microstate.
- (3) We imagine many virtual identical systems in the same macrostate. The set of virtual copies of systems corresponding to different microstates under external constraints is called a *statistical ensemble*. Macrostates are averages computed using **ensemble averages** where the probability of the system being in a microstate as the fraction of these imaginary systems that are in that state.
- (4) A system for which time averages and ensemble averages are equal is said to be *ergodic*.

- (5) The ensemble of isolated systems with the fixed volume  $V$ , the fixed number of particles  $N$ , and the fixed energy  $E$  is called **microcanonical ensemble**.



EXAMPLES:

A system has  $N = 4$  particles and the energy  $E = 14\epsilon_0$ .



The microstates of the configuration  $\{0, 1, 0, 3\}$  are

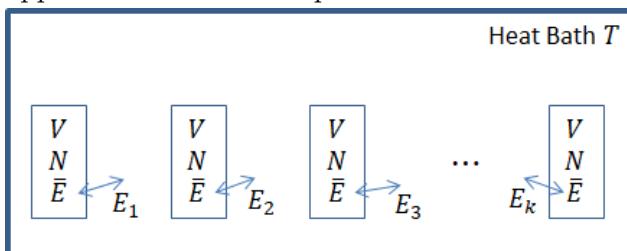
$$W(6\epsilon_0) = \frac{4!}{0! 1! 0! 3!} = 4$$

The microstates of the configuration  $\{0, 0, 2, 2\}$  are

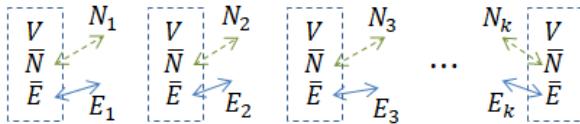
$$W(6\epsilon_0) = \frac{4!}{0! 0! 2! 2!} = 6$$

The microstates of the energy are  $W(E) = W(6\epsilon_0) = 10$

- (6) The ensemble of closed systems with the fixed volume  $V$  and fixed number of particles  $N$  thermally contacts to a heat reservoir to approach the thermal equilibrium is called **canonical ensemble**.



- (7) The ensemble of open systems with the fixed volume  $V$  and thermally contacts to a particle reservoir and heat reservoir to approach the thermal equilibrium is called **grand canonical ensemble**.



### C. BOLTZMANN DISTRIBUTION

- (1) An isolated system is divided into two independent subsystems as  $V = V_1 + V_2$ ,  $N = N_1 + N_2$ ,  $E = E_1 + E_2$ , and then put them together and forbid any exchange of energy between them.

$$E_1 \neq E_2$$

$E_1 \neq E_2$	
$V_1$	$V_2$
$N_1$	$N_2$
$E_1$	$E_2$

$$S_1(V_1, N_1, E_1) \quad S_2(V_2, N_2, E_2)$$

The total microstates are  $W = W_1(E_1) \times W_2(E_2)$

The total entropy is  $S = S_1 + S_2$

Assume that  $S = f(W)$ , therefore,  $S_1 = f(W_1)$  and  $S_2 = f(W_2)$

Since  $S_1 + S_2 = S$ ,

$$\Rightarrow f(W_1) + f(W_2) = f(W) = f(W_1 W_2)$$

$$\frac{\partial f(W_1)}{\partial W_1} = \frac{\partial f(W_1 W_2)}{\partial W_1} = \frac{\partial f(W_1 W_2)}{\partial(W_1 W_2)} \frac{\partial(W_1 W_2)}{\partial W_1} = W_2 f'(W_1 W_2)$$

Similarly,

$$\frac{\partial f(W_2)}{\partial W_2} = \frac{\partial f(W_1 W_2)}{\partial W_2} = \frac{\partial f(W_1 W_2)}{\partial(W_1 W_2)} \frac{\partial(W_1 W_2)}{\partial W_2} = W_1 f'(W_1 W_2)$$

$$\Rightarrow \frac{\frac{\partial f(W_1)}{\partial W_1}}{\frac{\partial f(W_2)}{\partial W_2}} = \frac{W_2 f'(W_1 W_2)}{W_1 f'(W_1 W_2)}$$

$$\Rightarrow W_1 \frac{\partial f(W_1)}{\partial W_1} = W_2 \frac{\partial f(W_2)}{\partial W_2} = \text{constant} = k_B$$

$$\Rightarrow \partial f(W_1) = k_B \frac{\partial W_1}{W_1} \text{ and } \partial f(W_2) = k_B \frac{\partial W_2}{W_2}$$

$$\Rightarrow f(W_1) = k_B \ln W_1 \text{ and } f(W_2) = k_B \ln W_2$$

$\Rightarrow S_1 = k_B \ln W_1$  and  $S_2 = k_B \ln W_2$  .....Boltzmann principle

- (2) When two subsystems exchange energy, the two subsystems will reach an equilibrium state and have the same energy  $\bar{E} = (E_1 + E_2)/2$ .

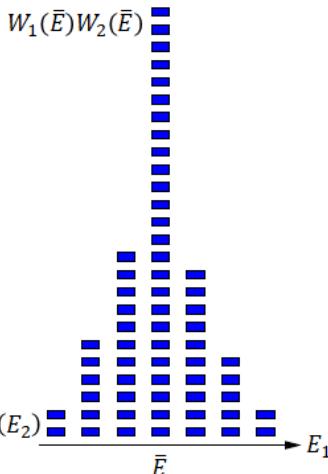
(a) Heat Bath  $T$

$V_1$	$V_2$
$N_1$	$N_2$
$\bar{E}$	$\bar{E}$

The total energy is  $E_1 + E_2 = 2\bar{E}$ .

The total microstates are

$$\bar{W} = \sum_{E_1} W_1(E_1)W_2(2\bar{E} - E_1)$$



After two systems reach the equilibrium, we forbid the energy exchange.

(b) Heat Bath  $T$

$V_1$	$V_2$
$N_1$	$N_2$
$\bar{E}$	$\bar{E}$

The total microstates are reduced to  $\bar{W}' = W_1(\bar{E})W_2(\bar{E})$  which is the maximum value of  $W_1(E_1)W_2(2\bar{E} - E_1)$ .

Since  $\bar{W}' > \frac{\bar{W}}{N}$  and  $\bar{W} > \bar{W}'$

$$\Rightarrow \ln \bar{W} > \ln \bar{W}' > \ln \left( \frac{\bar{W}}{N} \right)$$

where  $N$  is the number of possible distinct value of  $E_1$  and  $\bar{W}/N$  is the average value of  $\bar{W}$ .

Use Boltzmann principle

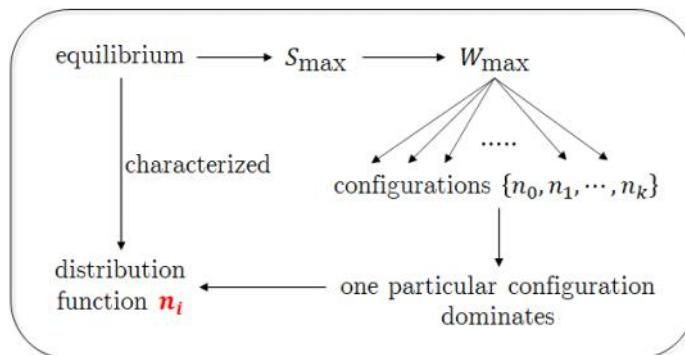
$$\Rightarrow \bar{S} > \bar{S}' > \bar{S} - k_B \ln N.$$

Since  $\bar{S} \sim O(N)$ , in the thermodynamic limit, i.e., large  $N$  limit,

$$\Rightarrow \bar{S} > \bar{S}' > \bar{S}$$

$$\Rightarrow \bar{S} = \bar{S}'$$

As the system goes to the equilibrium state, the entropy of the system is maximized. The thermal equilibrium state has the maximum entropy, i.e.,  $S_{\max} = k_B \ln W(\bar{E})$ .



$\Rightarrow$  The equilibrium of the system will be the characteristic of the particular dominating configuration.

- (3) As the energies  $E$  of systems fluctuate little about  $\bar{E}$ , each system can be considered as an isolated system. The canonical ensemble is approximated to the microcanonical ensembles. We adopt the microcanonical ensemble to derive the distribution  $n_i$  of the equilibrium configuration.

Determine the maximum value of  $\ln W$  consistent with a given total energy  $E$ , and a given total number of particles  $N$  by using the so-called Lagrange method of underdetermined multipliers.

$$E = \sum_i \varepsilon_i n_i$$

$$N = \sum_i n_i$$

Let  $f(n_1, \dots, n_k) = \ln W + \alpha \left( N - \sum_i n_i \right) + \beta \left( E - \sum_i \varepsilon_i n_i \right)$

For large  $N$ ,  $\ln W = N \ln N - \sum_i n_i \ln n_i$

$$f(n_1, \dots, n_k) = N \ln N + \alpha N + \beta E - \sum_i (n_i \ln n_i + \alpha n_i + \beta \varepsilon_i n_i)$$

Apply Fermat's theorem (stationary point)

$$\frac{\partial f}{\partial n_i} = -( \ln n_i + 1 ) - \alpha - \beta \varepsilon_i = 0$$

$$\Rightarrow \ln n_i = -1 - \alpha - \beta \varepsilon_i$$

$$\Rightarrow n_i = e^{-(1+\alpha)-\beta\varepsilon_i} = A e^{-\beta\varepsilon_i}$$

Normalization conditions to determine the unknown variable  $A$ :

$$N = \sum_i n_i = A \sum_i e^{-\beta\varepsilon_i} \Rightarrow A = \frac{N}{\sum_i e^{-\beta\varepsilon_i}}$$

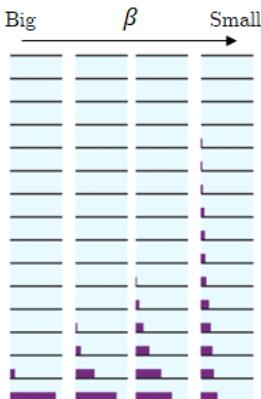
$$\Rightarrow n_i = \frac{N e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}} \text{.....Boltzmann distribution}$$

The denominator of this expression is denoted by  $Z$  and is called the **partition function**, i.e.,

$$Z = \sum_i e^{-\beta\varepsilon_i}$$

$Z$  measures how the total number of particles is distributed - partitioned - over the available states.



$$Z = 1.05 \quad 1.58 \quad 1.99 \quad 3.86$$

$$\Rightarrow n_i = \frac{N e^{-\beta \varepsilon_i}}{Z}$$

$$\Rightarrow p_i = \frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{Z}$$

### EXAMPLES:

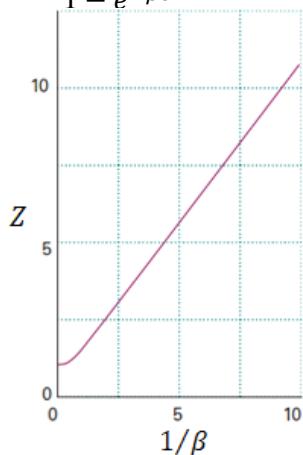
1. Consider an ensemble of  $N$  identical harmonic oscillators, each of them has an infinite number of equally spaced nondegenerate energy levels.

- (a) The partition function is

$$Z = 1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon} + \dots$$

$$= 1 + e^{-\beta \varepsilon} + (e^{-\beta \varepsilon})^2 + \dots$$

$$= \frac{1}{1 - e^{-\beta \varepsilon}}$$



(b) The internal energy is

$$\begin{aligned}
 E &= \sum_i n_i \varepsilon_i \\
 &= \sum_i \frac{N e^{-\beta \varepsilon_i}}{Z} \varepsilon_i \\
 &= \frac{N}{Z} \sum_i \left( -\frac{\partial}{\partial \beta} e^{-\beta \varepsilon_i} \right) \\
 &= -\frac{N}{Z} \frac{\partial}{\partial \beta} Z \\
 &= -N \frac{\partial}{\partial \beta} \ln Z
 \end{aligned}$$

Since  $\ln Z = -\ln(1 - e^{-\beta \varepsilon})$

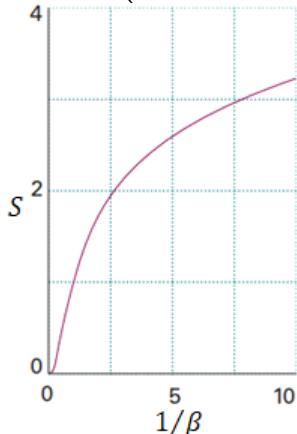
$$\begin{aligned}
 \Rightarrow \frac{\partial}{\partial \beta} \ln Z &= -\frac{\varepsilon e^{-\beta \varepsilon}}{1 - e^{-\beta \varepsilon}} = -\frac{\varepsilon}{e^{\beta \varepsilon} - 1} \\
 \Rightarrow E &= -N \left( -\frac{\varepsilon}{e^{\beta \varepsilon} - 1} \right) = \frac{N \varepsilon}{e^{\beta \varepsilon} - 1}
 \end{aligned}$$

(c) The entropy is

$$\begin{aligned}
 S &= k_B \ln W \\
 &= k_B \left( N \ln N - \sum_i n_i \ln n_i \right) \\
 &= k_B \left( \sum_i n_i \ln N - \sum_i n_i \ln n_i \right) \\
 &= -k_B \sum_i n_i \ln \frac{n_i}{N} \\
 &= -k_B N \sum_i p_i \ln p_i \dots \text{Shannon entropy}
 \end{aligned}$$

Since  $\ln p_i = \ln \frac{e^{-\beta \varepsilon_i}}{Z} = -\beta \varepsilon_i - \ln Z$

$$\begin{aligned}
S &= -Nk_B \sum_i p_i (-\beta \varepsilon_i - \ln Z) \\
&= \frac{1}{T} \sum_i n_i \varepsilon_i + Nk_B \ln Z \\
&= \frac{E}{T} + Nk_B \ln Z \\
&= -\frac{N}{T} \frac{\partial}{\partial \beta} \ln Z + Nk_B \ln Z \\
&= -\frac{N}{T} \left( -\frac{\varepsilon}{e^{\beta \varepsilon} - 1} \right) + Nk_B (-\ln(1 - e^{-\beta \varepsilon})) \\
&= Nk_B \left( \frac{\beta \varepsilon}{e^{\beta \varepsilon} - 1} - \ln(1 - e^{-\beta \varepsilon}) \right)
\end{aligned}$$



2. Free expansion is an irreversible process

$$S = k_B \ln W = -k_B N \sum_i p_i \ln p_i$$



(a) Close gate:

$$W = \frac{N!}{N! 0!} = 1$$

From Boltzmann principle:

$$S = \ln 1 = 0$$

From Shannon entropy:

$$\begin{aligned} S &= -k_B N_A p_A \ln p_A - k_B N_B p_B \ln p_B \\ &= -k_B N \ln 1 - k_B 0 \ln 0 \\ &= 0 \end{aligned}$$

(b) Open gate:

$$W = \frac{N!}{N/2! N/2!}$$

From Boltzmann principle:

$$\begin{aligned} S &= k_B \ln \frac{N!}{N/2! N/2!} \\ &= k_B \left( \ln N! - \ln \frac{N}{2}! - \ln \frac{N}{2}! \right) \\ &\approx k_B \left( N \ln N - N - \frac{N}{2} \ln \frac{N}{2} + \frac{N}{2} - \frac{N}{2} \ln \frac{N}{2} + \frac{N}{2} \right) \\ &= k_B \left( N \ln N - N \ln \frac{N}{2} \right) \\ &= k_B N \ln 2 \end{aligned}$$

From Shannon entropy:

$$\begin{aligned} S &= -k_B N_A p_A \ln p_A - k_B N_B p_B \ln p_B \\ &= -k_B N \frac{1}{2} \ln \frac{1}{2} - k_B N \frac{1}{2} \ln \frac{1}{2} \\ &= -k_B N \ln \frac{1}{2} \\ &= k_B N \ln 2 \end{aligned}$$

(c) entropy increase

$$\Delta S = k_B N \ln 2$$

(4) Determine  $\beta$

Take two subsystems in thermal contact, each with  $(V, N, E)$  macrostates.

$$\bar{W} = W_1(E_1)W_2(E_2) = W_1(E_1)W_2(E - E_1)$$

In thermal equilibrium, the total number of microstates of the combined system must be at a maximum, i.e.,

$$\frac{\partial \bar{W}}{\partial E_1} = 0$$

Since

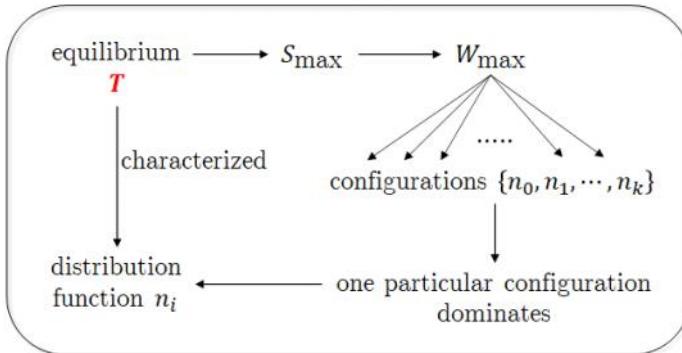
$$\begin{aligned}\frac{\partial \bar{W}}{\partial E_1} &= W_2 \frac{\partial W_1}{\partial E_1} + W_1 \frac{\partial W_2}{\partial E_1} = W_2 \frac{\partial W_1}{\partial E_1} + W_1 \frac{\partial W_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} = W_2 \frac{\partial W_1}{\partial E_1} - W_1 \frac{\partial W_2}{\partial E_2} \\ \Rightarrow W_2 \frac{\partial W_1}{\partial E_1} - W_1 \frac{\partial W_2}{\partial E_2} &= 0 \\ \Rightarrow \frac{1}{W_1} \frac{\partial W_1}{\partial E_1} &= \frac{1}{W_2} \frac{\partial W_2}{\partial E_2} \\ \Rightarrow \frac{\partial \ln W_1}{\partial E_1} &= \frac{\partial \ln W_2}{\partial E_2} = \text{constant} = \beta \dots \dots \text{(a)}\end{aligned}$$

We also know that

$$\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} \dots \dots \text{(b)}$$

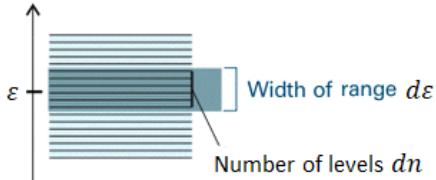
$$\frac{(b)}{(a)} = \frac{\partial S}{\partial \ln W} = \frac{1}{\beta T} = \text{constant} = k_B$$

$$\Rightarrow \beta = \frac{1}{k_B T}$$



## D. DENSITY OF STATES

- (1) For systems of a large size and thus very finely quantized energy levels,



the summation in the partition function is replaced by integration as,

$$Z = \sum_i e^{-\beta \varepsilon_i} = \int e^{-\beta \varepsilon} g(\varepsilon) d\varepsilon$$

where  $g(\varepsilon)$  is called the density of states.

One can define the density of states  $g(\varepsilon)$  as the number of energy levels  $dn$  in the interval  $d\varepsilon$ , i.e.,

$$dn = g(\varepsilon)d\varepsilon$$

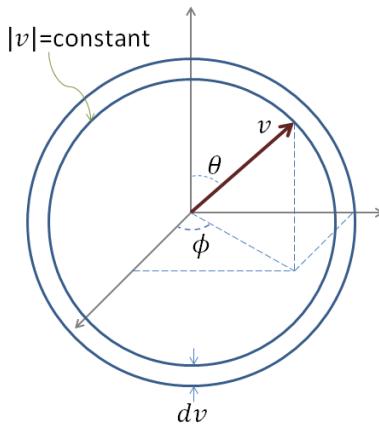
- (2) The number of particles in the energy interval  $d\varepsilon$  is the product of the number of particles in one energy level  $n(\varepsilon)$  and the number of energy levels in this energy interval  $dn$ ,

$$dN(\varepsilon) = n(\varepsilon)dn = n(\varepsilon)g(\varepsilon)d\varepsilon = \frac{Ne^{-\beta\varepsilon}}{Z}g(\varepsilon)d\varepsilon$$

EXAMPLES:

1. Maxwell velocity distribution:

For an ideal gas, the energy  $\varepsilon = \frac{1}{2}mv^2$  is a continuous variable and only depends upon the radius  $v$ .



The density of states between  $v$  and  $v + dv$  is a spherical shell,

$$dn = 4\pi v^2 dv = g(v)dv$$

$$\Rightarrow g(v) = 4\pi v^2$$

$$Z = \int e^{-\beta\varepsilon} g(v) dv = \int 4\pi v^2 e^{-\frac{\beta}{2}mv^2} dv = \left(\frac{2\pi}{\beta m}\right)^{3/2}$$

The number of particles in the speed interval  $dv$

$$dN(v) = n(v)dn = \frac{Ne^{-\beta\varepsilon}}{Z}g(v)dv$$

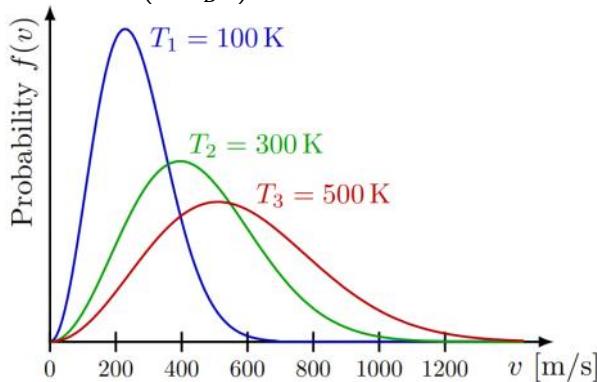
$$\Rightarrow \frac{dN(v)}{N} = f(v)dv$$

where the speed distribution function is

$$f(v)dv = \frac{e^{-\beta\varepsilon}}{Z} g(v)dv = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{\beta}{2}mv^2} 4\pi v^2 dv$$

Since

$$\begin{aligned} \int_0^\infty f(v) dv &= \int_0^\infty \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{\beta}{2}mv^2} 4\pi v^2 dv = 1 \\ \Rightarrow f(v)dv &= \underbrace{\left(\frac{\beta m}{2\pi}\right)^{3/2}}_{\substack{\text{Normalization} \\ \text{constant}}} \underbrace{e^{-\frac{\beta}{2}mv^2}}_{\substack{\text{Boltzmann} \\ \text{factor}}} \underbrace{4\pi v^2 dv}_{\text{Volume of speed space}} \\ \Rightarrow f(v) &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/2k_B T} \end{aligned}$$



where  $T_3 > T_2 > T_1$

OS:

[Maxwell-Boltzmann distribution – TikZ.net](#)

2. An explanation of an upward shift in the entire graph:  
Since  $d\varepsilon = mvdv$

$$\begin{aligned} dn &= 4\pi \frac{v}{m} d\varepsilon = 4\pi \frac{\sqrt{2\varepsilon}}{m^{3/2}} d\varepsilon = g(\varepsilon) d\varepsilon \\ \Rightarrow g(\varepsilon) &= 4\pi \frac{\sqrt{2\varepsilon}}{m^{3/2}} \end{aligned}$$

$$\begin{aligned}
Z &= \int e^{-\beta\varepsilon} g(\varepsilon) d\varepsilon \\
&= 4\pi \frac{\sqrt{2}}{m^{3/2}} \int e^{-\beta\varepsilon} \sqrt{\varepsilon} d\varepsilon \\
&= 4\pi \frac{\sqrt{2}}{m^{3/2}} \times \frac{\sqrt{\pi}}{2\beta^{3/2}} \\
&= \left( \frac{2\pi}{\beta m} \right)^{3/2}
\end{aligned}$$

The Maxwell distribution function is

$$\begin{aligned}
f(\varepsilon) d\varepsilon &= \frac{e^{-\beta\varepsilon}}{Z} g(\varepsilon) d\varepsilon \\
&= \frac{e^{-\beta\varepsilon}}{\left( \frac{2\pi}{\beta m} \right)^{3/2}} \times 4\pi \frac{\sqrt{2\varepsilon}}{m^{3/2}} \times d\varepsilon \\
&= \left( \frac{\beta}{\pi} \right)^{3/2} 2\pi\sqrt{\varepsilon} e^{-\beta\varepsilon} d\varepsilon
\end{aligned}$$

The average kinetic energy is

$$\begin{aligned}
\langle E \rangle &= \int_0^\infty \varepsilon f(\varepsilon) d\varepsilon \\
&= \int_0^\infty \varepsilon \left( \frac{\beta}{\pi} \right)^{3/2} 2\pi\sqrt{\varepsilon} e^{-\beta\varepsilon} d\varepsilon \\
&= \left( \frac{1}{\pi} \right)^{3/2} 2\pi \times \frac{1}{\beta} \int_0^\infty (\beta\varepsilon)^{3/2} e^{-(\beta\varepsilon)} d(\beta\varepsilon)
\end{aligned}$$

$$\text{Let } x = \sqrt{\beta\varepsilon}$$

$$\begin{aligned}
\langle E \rangle &= \left( \frac{1}{\pi} \right)^{3/2} 2\pi \times \frac{1}{\beta} \int_0^\infty x^3 e^{-x^2} dx^2 \\
&= \left( \frac{1}{\pi} \right)^{3/2} 2\pi \times \frac{2}{\beta} \int_0^\infty x^4 e^{-x^2} dx \\
&= \left( \frac{1}{\pi} \right)^{3/2} 2\pi \times \frac{2}{\beta} \times \frac{3}{8} \sqrt{\pi} \\
&= \frac{3}{2} k_B T
\end{aligned}$$

Since

$$\langle E \rangle = \int_0^\infty \frac{1}{2} mv^2 f(v) dv = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

where  $\sqrt{\overline{v^2}} \equiv \sqrt{\langle v^2 \rangle}$  is called root-mean-square speed.

⇒ The root-mean-square speed of molecules is the speed at which all the molecules have the same average kinetic energy as in case of their actual speed.

⇒ Increasing the temperature of a gas increases the average kinetic energy of its particles, i.e., a higher number of particles having higher energies, which in turn shifts the graph to the right.

3. An explanation of the broadening of the curve:

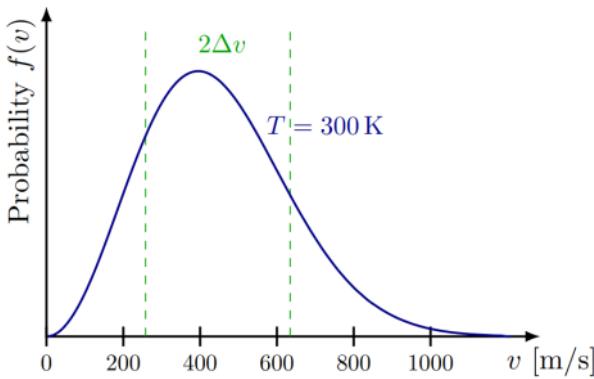
The width of the curve is  $(\Delta v)^2 = \langle v^2 \rangle - \langle v \rangle^2$

Since

$$\begin{aligned}\langle v^2 \rangle &= \int_0^\infty v^2 f(v) dv \\&= 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2k_B T} dv \\&= \frac{3k_B T}{m} \\ \langle v \rangle &= \int_0^\infty v f(v) dv \\&= 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2k_B T} dv \\&= \frac{8k_B T}{\pi m}\end{aligned}$$

Thus, we obtain

$$(\Delta v)^2 = \langle v^2 \rangle - \langle v \rangle^2 = \frac{3k_B T}{m} - \frac{8k_B T}{\pi m} \simeq 0.45 \frac{k_B T}{m}$$



⇒ Increasing the temperature of a gas causes a broader curve.

4. An explanation of peak shift:

Most probable speed:

$$\frac{df(v)}{dv} = \left( \frac{m}{2\pi k_B T} \right)^{3/2} 4\pi \left( 2v - \frac{mv^2}{k_B T} \right) e^{-mv^2/2k_B T} = 0$$

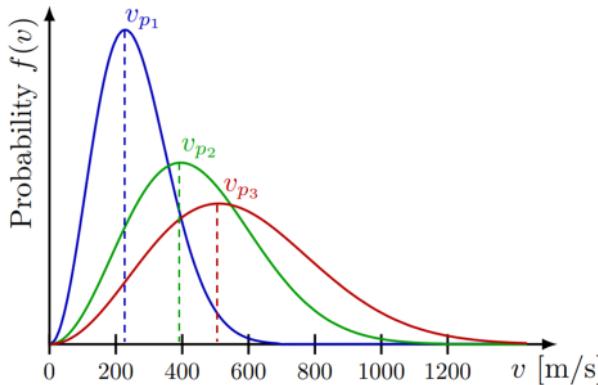
$$\Rightarrow v_p = \sqrt{\frac{2k_B T}{m}}$$

⇒ With increase of temperature, the most probable speed increases.

Since

$$f(v_p) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} 4\pi \frac{2k_B T}{m} e^{-1} = \frac{4}{e} \sqrt{\frac{m}{2\pi k_B T}}$$

⇒ With increase of temperature, the fractions of molecules possessing most probable speed decreases.



## 3-2 Distribution of Quantum Particles

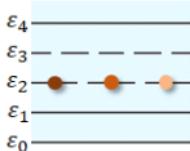
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### A. BOSE-EINSTEIN DISTRIBUTION FUNCTION

- (1) Suppose we have a number of energy levels, labelled by index  $i$ , each level having energy  $\varepsilon_i$  with degeneracies  $g_i$  and containing a total of  $n_i$  indistinguishable particles. Each sublevel are distinguishable.

EXAMPLES:

The microstates of distributing 3 particles to energy level  $\varepsilon_2$  with degeneracies 3 are



The following methods are equivalent:

- (a) Listing all combinations

3	0	0
0	3	0
0	0	3
2	1	0
2	0	1
1	2	0
0	2	1
1	0	2
0	1	2
1	1	1

- (b) The number of non-negative integer solutions of the equation:

$$x + y + z = 3$$

$(3, 0, 0), (0, 3, 0), (0, 0, 3)$

$(2, 1, 0), (2, 0, 1), (1, 2, 0), (0, 2, 1), (1, 0, 2), (0, 1, 2)$

$(1, 1, 1)$

- (c) Each possible solution in an arrangement of 3 balls and 2 plus signs, i.e.,  $\bullet\bullet+\bullet+$

The number of arrangement is

$$C_3^5 = \frac{5!}{3! 2!} = 10$$

(d) Combination with Repetition formula

$$H_3^3 = C_3^{3+3-1} = C_3^5 = 10$$

- (2) In general, the microstates of distributing  $n_i$  particles to energy level  $\varepsilon_i$  with degeneracies  $g_i$  are

$$H_{n_i}^{g_i} = C_{n_i}^{n_i + g_i - 1} = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

The microstates for all possible energy levels are

$$W = \prod_i C_{n_i}^{n_i + g_i - 1} = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

Determine the maximum value of  $\ln W$  consistent with a given total energy  $E$ , and a given total number of particles  $N$  by using the so-called Lagrange method of underdetermined multipliers.

$$\text{Let } f(n_1, \dots, n_k) = \ln W + \alpha \left( N - \sum_i n_i \right) + \beta \left( E - \sum_i \varepsilon_i n_i \right)$$

$$\text{For large } N \text{ and } g_i, W \approx \prod_i \frac{(n_i + g_i)!}{n_i! g_i!}$$

$$\begin{aligned} \ln W &\approx \sum_i (n_i + g_i) \ln(n_i + g_i) - \sum_i (n_i + g_i) \\ &\quad - \sum_i n_i \ln n_i + \sum_i n_i - \sum_i g_i \ln g_i + \sum_i g_i \\ &= \sum_i (n_i + g_i) \ln(n_i + g_i) - \sum_i n_i \ln n_i - \sum_i g_i \ln g_i \end{aligned}$$

$$\begin{aligned} f(n_1, \dots, n_k) &= \sum_i \left( (n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i \right) \\ &\quad + \alpha N + \beta E - \sum_i (\alpha n_i + \beta \varepsilon_i n_i) \end{aligned}$$

Apply Fermat's theorem (stationary point)

$$\begin{aligned} \frac{\partial f}{\partial n_i} &= \ln(n_i + g_i) + 1 - (\ln n_i + 1) - (\alpha + \beta \varepsilon_i) = 0 \\ \Rightarrow \ln(n_i + g_i) - \ln n_i &= \alpha + \beta \varepsilon_i \end{aligned}$$

$$\Rightarrow \ln \frac{n_i + g_i}{n_i} = \alpha + \beta \varepsilon_i$$

$$\Rightarrow n_i + g_i = n_i e^{\alpha + \beta \varepsilon_i}$$

$$\Rightarrow n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} - 1}$$

$\beta$  can, as usual, be related to the thermodynamic temperature.

- (3) Determine unknown variable  $\alpha$

Since the total number  $N$  of bosons is not conserved, they can be created or annihilated in course of interactions. The constraint that the total number of particles is constant can be lifted by setting  $\alpha = 0$ .

$$\Rightarrow n_i = \frac{g_i}{e^{\varepsilon_i/k_B T} - 1} \dots \text{Bose-Einstein distribution}$$

- (4) A collection of indistinguishable particles, satisfying the Bose-Einstein distribution, are called bosons.

$$\frac{n_i}{g_i} = \frac{1}{e^{\varepsilon_i/k_B T} - 1}$$

If  $\varepsilon_i \ll k_B T$ ,  $e^{\varepsilon_i/k_B T} - 1 \rightarrow 0$

$$\Rightarrow \frac{n_i}{g_i} \gg 1$$

$$\Rightarrow n_i \gg g_i$$

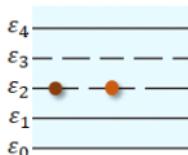
$\Rightarrow$  It is possible for many identical bosons to exist in the same energy level.

## B. FERMI-DIRAC DISTRIBUTION FUNCTION

- (1) Suppose we have a number of energy levels, labelled by index  $i$ , each level having energy  $\varepsilon_i$  with degeneracies  $g_i$  and containing a total of  $n_i$  indistinguishable particles satisfying the Pauli exclusion principle.

EXAMPLES:

The microstates of distributing 2 particles to energy level  $\varepsilon_2$  with degeneracies 3 are



$$C_2^3 = \frac{3!}{2! 1!} = 3$$

- (2) In general, the microstates of distributing  $n_i$  particles to energy level  $\varepsilon_i$  with degeneracies  $g_i$  and satisfying the Pauli exclusion principle are

$$C_{n_i}^{g_i} = \frac{g_i!}{n_i! (g_i - n_i)!}$$

The microstates for all possible energy levels are

$$W = \prod_i C_{n_i}^{g_i} = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}$$

Determine the maximum value of  $\ln W$  consistent with a given total energy  $E$ , and a given total number of particles  $N$  by using the so-called Lagrange method of underdetermined multipliers.

$$\text{Let } f(n_1, \dots, n_k) = \ln W + \alpha \left( N - \sum_i n_i \right) + \beta \left( E - \sum_i \varepsilon_i n_i \right)$$

For large  $N$  and  $g_i$ ,

$$\begin{aligned} \ln W &\approx \sum_i g_i \ln g_i - \sum_i g_i - \sum_i n_i \ln n_i + \sum_i n_i \\ &\quad - \sum_i (g_i - n_i) \ln(g_i - n_i) + \sum_i (g_i - n_i) \\ &= \sum_i g_i \ln g_i - \sum_i n_i \ln n_i - \sum_i (g_i - n_i) \ln(g_i - n_i) \end{aligned}$$

$$\begin{aligned} f(n_1, \dots, n_k) &= \sum_i (g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i)) \\ &\quad + \alpha N + \beta E - \sum_i (\alpha n_i + \beta \varepsilon_i n_i) \end{aligned}$$

Apply Fermat's theorem (stationary point)

$$\frac{\partial f}{\partial n_i} = -(\ln n_i + 1) - (-\ln(g_i - n_i) - 1) - (\alpha + \beta \varepsilon_i) = 0$$

$$\Rightarrow -\ln n_i + \ln(g_i - n_i) = \alpha + \beta \varepsilon_i$$

$$\Rightarrow \ln \frac{g_i - n_i}{n_i} = \alpha + \beta \varepsilon_i$$

$$\Rightarrow g_i - n_i = n_i e^{\alpha + \beta \varepsilon_i}$$

$$\Rightarrow n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1}$$

- (3) Determine unknown variables  $\alpha$  and  $\beta$

The first law of thermodynamics gives

$$dE = TdS + \mu dN = k_B T d(\ln W) + \mu dN$$

Since

$$\begin{aligned} d(\ln W) &= d\left(\sum_i g_i \ln g_i - \sum_i n_i \ln n_i - \sum_i (g_i - n_i) \ln(g_i - n_i)\right) \\ &= d\left(\sum_i g_i \ln g_i - \sum_i n_i \ln n_i - \sum_i (g_i - n_i)(\ln n_i + \ln e^{\alpha+\beta\varepsilon_i})\right) \\ &= d\left(\sum_i g_i \ln \frac{g_i}{n_i} - \sum_i (g_i - n_i) \ln e^{\alpha+\beta\varepsilon_i}\right) \\ &\approx d\left(\sum_i g_i \ln e^{\alpha+\beta\varepsilon_i} - \sum_i (g_i - n_i) \ln e^{\alpha+\beta\varepsilon_i}\right) \\ &= d\left(\sum_i n_i \ln e^{\alpha+\beta\varepsilon_i}\right) \\ &= \alpha dN + \beta dE \\ \Rightarrow dE &= \frac{1}{\beta} d(\ln W) - \frac{\alpha}{\beta} dN \\ \Rightarrow \beta &= \frac{1}{k_B T} \text{ and } \alpha = -\frac{\mu}{k_B T} \text{ where } \mu \text{ is the chemical potential} \\ \Rightarrow n_i &= \frac{g_i}{e^{(\varepsilon_i-\mu)/k_B T} + 1} \dots \text{Fermi-Dirac distribution} \end{aligned}$$

- (4) A collection of indistinguishable particles, satisfying the Fermi-Dirac distribution, are called fermions.

$$\frac{n_i}{g_i} = \frac{1}{e^{(\varepsilon_i-\mu)/k_B T} + 1}$$

Since  $e^{(\varepsilon_i-\mu)/k_B T} > 0$  for all energy levels,  $e^{(\varepsilon_i-\mu)/k_B T} + 1 > 1$ .

$$\Rightarrow \frac{n_i}{g_i} < 1$$

$$\Rightarrow n_i < g_i$$

$\Rightarrow$  Fermions always obey the Pauli exclusion principle.

### 3-3 Density of States

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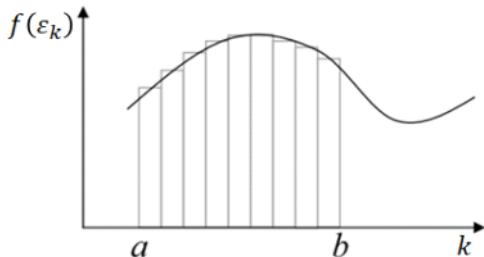
#### A. DENSITY OF STATES (DOS)

- (1) For some physical quantities, we need to evaluate

$$\sum_k f(\varepsilon_k)$$

where  $f(\varepsilon_k)$  is a function of  $\varepsilon_k$  (energy band).

Adopt the definition of the integral, we have



$$\sum_k f(\varepsilon_k) \Delta^3 k = \int f(\varepsilon_k) d^3 k \Rightarrow \sum_k f(\varepsilon_k) = \frac{1}{\Delta^3 k} \int f(\varepsilon_k) d^3 k$$

The allowed discrete  $\vec{k}$  values in the first Brillouin zone are given by

$$\vec{k} = \frac{\ell_1}{N_1} \vec{b}_1 + \frac{\ell_2}{N_2} \vec{b}_2 + \frac{\ell_3}{N_3} \vec{b}_3, \text{ and } -\frac{N_i}{2} \leq \ell_i < \frac{N_i}{2}$$

The volume element contains one  $\vec{k}$ -point is

$$\Delta^3 k = \left( \frac{2\pi}{N_x a} \right) \left( \frac{2\pi}{N_y a} \right) \left( \frac{2\pi}{N_z a} \right) = \frac{2\pi}{L_x} \frac{2\pi}{L_y} \frac{2\pi}{L_z} = \frac{(2\pi)^3}{V}$$

The summations over  $\vec{k}$  can be converted to integrals as follows:

$$\sum_k f(\varepsilon_k) = \frac{V}{(2\pi)^3} \int f(\varepsilon_k) d^3 k \dots \text{(a)}$$

OS:

Alternative thought:

$$\sum_k = \left( \frac{L}{2\pi} \right)^d \sum_k \left( \frac{2\pi}{L} \right)^d = \frac{V}{(2\pi)^d} \sum_k d^d k = \frac{V}{(2\pi)^d} \int d^d k$$

- (2) Alternatively, it is convenient to replace the sum over  $\vec{k}$ -points in the

first Brillouin zone by an integral over  $\varepsilon$ .

$$\text{Let } f(\varepsilon_k) = \int f(\varepsilon) \delta(\varepsilon - \varepsilon_k) d\varepsilon$$

$$\sum_k f(\varepsilon_k) = \int \sum_k f(\varepsilon) \delta(\varepsilon - \varepsilon_k) d\varepsilon$$

$$\text{Define } g(\varepsilon) = \frac{1}{V} \sum_k \delta(\varepsilon - \varepsilon_k)$$

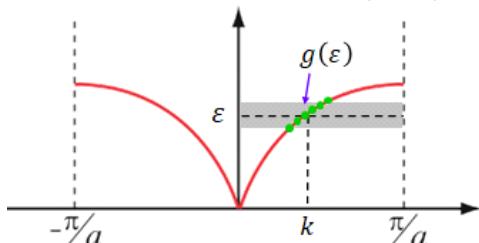
$$\sum_k f(\varepsilon_k) = V \int f(\varepsilon) g(\varepsilon) d\varepsilon \dots \dots \text{(b)}$$

Put (a) and (b) together, we obtain

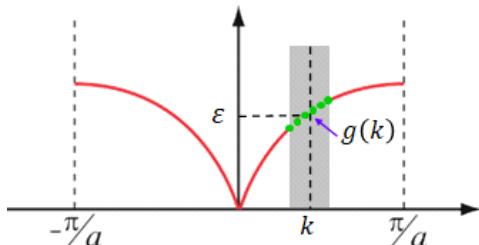
$$\frac{1}{V} \sum_k f(\varepsilon_k) = \frac{1}{(2\pi)^3} \int f(\varepsilon_k) d^3k = \int f(\varepsilon) g(\varepsilon) d\varepsilon$$

$$(3) \quad g(\varepsilon) = \frac{1}{V} \sum_k \delta(\varepsilon - \varepsilon_k)$$

is the number of states  $k$  per unit volume per interval  $d\varepsilon$  around  $\varepsilon$  and called the density of states (DOS).



Alternatively, we can define  $g(k)$  is the number of states  $\varepsilon$  per unit volume per interval  $dk$  around  $k$ ,



Thus, we have  $g(\varepsilon)d\varepsilon = g(k)dk$

## B. EVALUATE DENSITY OF STATES

(1) Direct integral approach:

$$g(\varepsilon) = \frac{1}{V} \sum_k \delta(\varepsilon - \varepsilon_k) = \frac{1}{(2\pi)^3} \int f(\varepsilon_k) d^3k$$

(2) Equal partition approach: each unit volume contains the same number of states

$$g(\varepsilon) = \frac{1}{(2\pi)^3} \int f(\varepsilon_k) d^3k$$

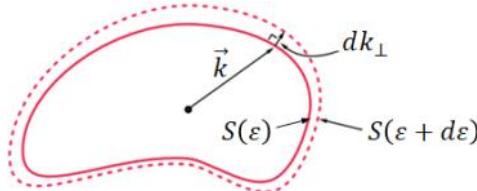
$$\text{Since } \frac{d^3k}{(2\pi)^3} = \frac{1}{V} \frac{d^3k}{(2\pi)^3/V} = \frac{1}{V} dN(\varepsilon_k)$$

where  $(2\pi)^3/V$  is the volume in  $\vec{k}$ -space a state occupied.

$$\begin{aligned} g(\varepsilon) &= \frac{1}{V} \int \delta(\varepsilon - \varepsilon_k) dN(\varepsilon_k) \\ &= \frac{1}{V} \int \delta(\varepsilon - \varepsilon_k) \frac{dN(\varepsilon_k)}{d\varepsilon_k} d\varepsilon_k \\ &= \frac{1}{V} \frac{dN(\varepsilon)}{d\varepsilon} \end{aligned}$$

(3) Surface integral approach:

Let  $S(\varepsilon)$  be the surface in  $\vec{k}$ -space on which  $\varepsilon_k$  has the value  $\varepsilon$ .



The energy change  $d\varepsilon$  in going from the surface  $S(\varepsilon)$  to the surface  $S(\varepsilon + d\varepsilon)$  can be expressed in terms of  $d\vec{k}$ , an infinitesimal displacement in  $\vec{k}$ -space, as

$$d\varepsilon = d\vec{k} \cdot \nabla_k \varepsilon = dk_{\perp} |\nabla_k \varepsilon|$$

The volume element  $d^3k$  in  $\vec{k}$ -space can be written as

$$d^3k = dS dk_{\perp} = \frac{dS}{|\nabla_k \varepsilon|} dk_{\perp}$$

$$g(\varepsilon) = \frac{1}{(2\pi)^3} \iint \delta(\varepsilon - \varepsilon_k) \frac{dS}{|\nabla_k \varepsilon|} d\varepsilon = \frac{1}{(2\pi)^3} \int \frac{dS}{|\nabla_k \varepsilon|}$$

where  $\nabla_k \varepsilon_k = \frac{\partial \varepsilon_k}{\partial \vec{k}} = \vec{v}_g$  is the group velocity.

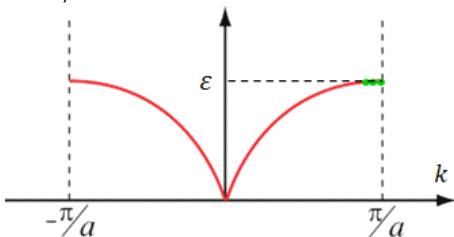
## C. VAN HOVE SINGULARITY (1953)

- (1) For  $\nabla_k \varepsilon_k = 0 \Rightarrow \varepsilon_k = \text{constant}$ ,  $\varepsilon_k$  is called flat band.

Flat band usually appears at the center of the Brillouin zone, the zone boundaries, or along high symmetry directions.

EXAMPLES:

$$\varepsilon_{k=\pi/a} = \text{constant}$$



- (2) From the surface integral,

$$g(\varepsilon) = \frac{1}{(2\pi)^3} \int \frac{dS}{|\nabla_k \varepsilon_k|}$$

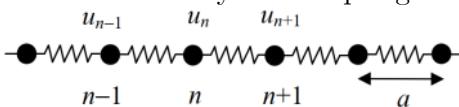
For flat bands  $\nabla_k \varepsilon_k = 0$ , the integrand exists singularities. Those singularities are called van Hove singularity. The density of states  $g(\varepsilon)$  has large value at flat bands.

# 4-1 Wave Properties of Sound

Tuesday, December 20, 2011 8:26 PM

## A. ONE ATOMIC LINEAR CHAIN WITH NEAREST NEIGHBOR INTERACTIONS

- (1) Suppose that there are  $N$  identical atoms of mass  $M$  in the lattice interconnected by elastic springs with the spring constant  $K$ .

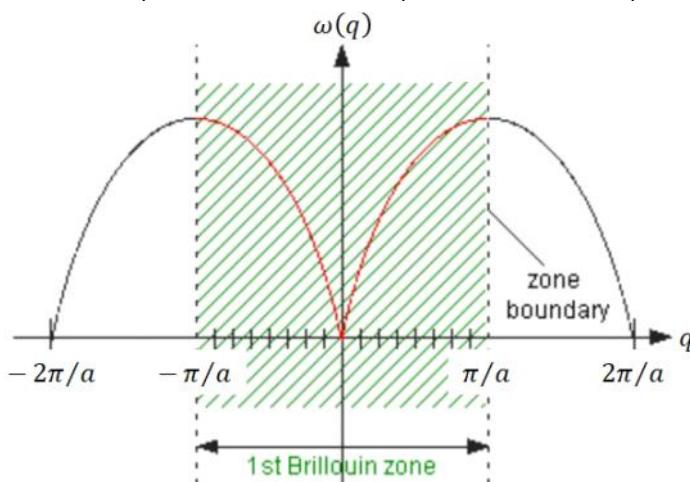


Applying Hooke's law to the motion of the  $n$ -th atom we obtain

$$\begin{aligned} M\ddot{u}_n &= -K(u_n - u_{n+1}) + K(u_{n-1} - u_n) \\ &= K(u_{n+1} + u_{n-1} - 2u_n) \dots\dots (a) \end{aligned}$$

Choose a trial function  $u_n = u_q e^{i(qna - \omega t)}$  and substitute into equation (a), we obtain

$$\begin{aligned} -M\omega^2 u_q e^{iqna} e^{-i\omega t} &= K(u_q e^{iq(n+1)a} + u_q e^{iq(n-1)a} - 2u_q e^{iqna}) e^{-i\omega t} \\ \Rightarrow -M\omega^2 u_q e^{iqna} &= K(u_q e^{iq(n+1)a} + u_q e^{iq(n-1)a} - 2u_q e^{iqna}) \\ \Rightarrow -M\omega^2 &= K(e^{iqa} + e^{-iqa} - 2) = K(2 \cos qa - 2) = 2K(\cos qa - 1) \\ \Rightarrow \omega(q) &= \sqrt{\frac{2K}{M}(1 - \cos qa)} = \sqrt{\frac{2K}{M} 2 \sin^2 \frac{qa}{2}} = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{qa}{2} \right| \end{aligned}$$



The first Brillouin zone:  $-\frac{\pi}{a} \leq q < \frac{\pi}{a}$

(2) Properties of the energy band:

1. Apply periodic boundary conditions:  $u_{N+1} = u_1$

$$u_{N+1} = u_q e^{i(q(N+1)a - \omega t)} = e^{iqNa} \underbrace{u_q e^{i(qa - \omega t)}}_{u_1} = u_1$$

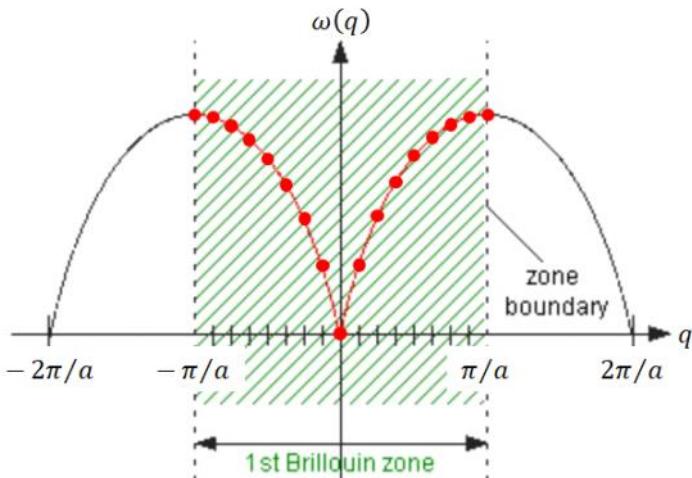
$$\Rightarrow e^{iqNa} = 1$$

$$\Rightarrow qNa = 2\pi\ell \text{ where } \ell = \text{integer}$$

$$\Rightarrow q = \frac{2\pi\ell}{Na}$$

$$\Rightarrow \Delta q = \frac{2\pi}{Na}$$

$\Rightarrow q$  is *discretized*. When  $N$  is taken to infinity (thermodynamic limit),  $\Delta q \rightarrow 0$ , the  $q$  values tend to a continuum.



2. Number of  $q$  values

Suppose that  $q$  is restricted to the first Brillouin zone, i.e.,

$$-\frac{\pi}{a} \leq q < \frac{\pi}{a} \Rightarrow -\frac{\pi}{a} \leq \frac{2\pi\ell}{Na} < \frac{\pi}{a} \Rightarrow -\frac{N}{2} \leq \ell < \frac{N}{2}$$

$\Rightarrow$  The total number of  $q$  values in the first Brillouin zone is  $N$ .

3. At zone boundary ( $q \rightarrow \pi/a$ )

$$\omega(q) = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{qa}{2} \right| = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{\pi}{2} \right| = 2 \sqrt{\frac{K}{M}}$$

$$v_{\text{group}} = \left| \frac{d\omega}{dq} \right| = 0$$

$\Rightarrow$  The modes at  $q = \pi/a$  do not transfer energy.

$\Rightarrow$  No energy transfer implies the elastic scattering  $|\vec{k}'| = |\vec{k}|$  of the X-ray.

$\Rightarrow$  Bragg diffraction of the X-ray

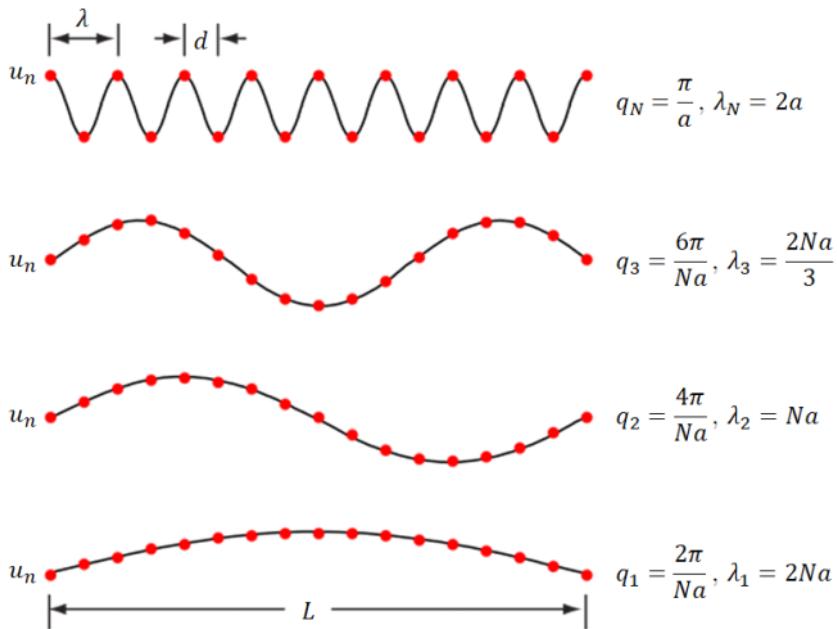
4. Near zone center ( $q \rightarrow 0$ , i.e., long wavelength limit)

$$\omega(q) = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{qa}{2} \right| \approx 2 \sqrt{\frac{K}{M}} \frac{qa}{2} = \sqrt{\frac{K}{M}} qa = vq$$

$$v_{\text{group}} = \left| \frac{d\omega}{dq} \right| = v$$

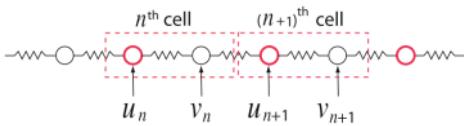
where  $v = \sqrt{\frac{K}{M}} a$  is the sound velocity.

- (3) Structure of vibrations:



## B. DIATOMIC LINEAR CHAIN WITH NEAREST NEIGHBOR INTERACTIONS

- (1) Suppose that there are  $N$  atoms of mass  $M_1$  and  $M_2$  in the lattice interconnected by elastic springs with the spring constant  $K$ .



Here  $u_n$  has mass  $M_1$  and  $v_n$  has mass  $M_2$

Applying Hooke's law to the motion of the  $n$ -th atom we obtain

$$M_1 \ddot{u}_n = K(v_n - u_n) + K(v_{n-1} - u_n) = K(v_n + v_{n-1} - 2u_n) \dots \text{(a)}$$

$$M_2 \ddot{v}_n = K(u_{n+1} - v_n) + K(u_n - v_n) = K(u_{n+1} + u_n - 2v_n) \dots \text{(b)}$$

Choose trial functions  $u_n = u_q e^{iqn2a - i\omega t}$  and  $v_n = v_q e^{iq(n2a+a) - i\omega t}$  and substitute into equation (a) and (b), we obtain

$$\begin{cases} -M_1 \omega^2 u_q e^{iqn2a} = K(v_q e^{iq(n2a+a)} + v_q e^{iq((n-1)2a+a)} - 2u_q e^{iqn2a}) \\ -M_2 \omega^2 v_q e^{iq(n2a+a)} = K(u_q e^{iq(n+1)2a} + u_q e^{iqn2a} - 2v_q e^{iq(n2a+a)}) \end{cases}$$

$$\Rightarrow \begin{cases} -M_1 \omega^2 u_q = K(v_q e^{iqa} + v_q e^{-iqa} - 2u_q) = 2K(v_q \cos qa - u_q) \\ -M_2 \omega^2 v_q = K(u_q e^{iqa} + u_q e^{-iqa} - 2v_q) = 2K(u_q \cos qa - v_q) \end{cases}$$

$$\Rightarrow \begin{pmatrix} 2K - M_1 \omega^2 & -2K \cos qa \\ -2K \cos qa & 2K - M_2 \omega^2 \end{pmatrix} \begin{pmatrix} u_q \\ v_q \end{pmatrix} = 0$$

The eigenvalues are given

$$(2K - M_1 \omega^2)(2K - M_2 \omega^2) - 4K^2 \cos^2 qa = 0$$

$$\Rightarrow M_1 M_2 \omega^4 - 2K(M_1 + M_2)\omega^2 + 4K^2 - 4K^2 \cos^2 qa = 0$$

$$\Rightarrow M_1 M_2 \omega^4 - 2K(M_1 + M_2)\omega^2 + 4K^2 \sin^2 qa = 0$$

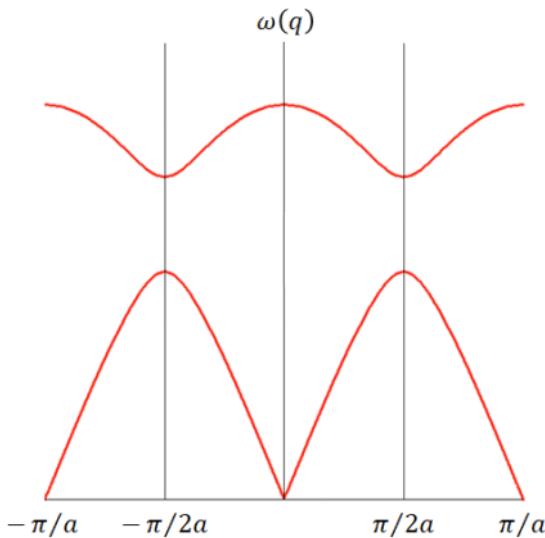
$$\omega^2(q) = \frac{1}{2M_1 M_2} \left( 2K(M_1 + M_2) \pm \sqrt{4K^2(M_1 + M_2)^2 - 4M_1 M_2 4K^2 \sin^2 qa} \right)$$

$$= \frac{1}{2M_1 M_2} \left( 2K(M_1 + M_2) \pm 2K \sqrt{(M_1 + M_2)^2 - 4M_1 M_2 \sin^2 qa} \right)$$

$$= \frac{K}{M_1 M_2} \left( M_1 + M_2 \pm \sqrt{(M_1 + M_2)^2 - 4M_1 M_2 \sin^2 qa} \right)$$

$$\omega_2^2(q) = \frac{K}{M_1 M_2} \left( M_1 + M_2 + \sqrt{(M_1 + M_2)^2 - 4M_1 M_2 \sin^2 qa} \right)$$

$$\omega_1^2(q) = \frac{K}{M_1 M_2} \left( M_1 + M_2 - \sqrt{(M_1 + M_2)^2 - 4M_1 M_2 \sin^2 qa} \right)$$



The first Brillouin zone:  $-\frac{\pi}{2a} \leq q < \frac{\pi}{2a}$

## (2) Properties of the energy bands:

1. Band gap at  $q = \pi/2a$

$$\Delta\omega = \omega_2 - \omega_1 = \sqrt{\frac{2K}{M_1}} - \sqrt{\frac{2K}{M_2}}$$

2. Number of  $q$  values

Apply periodic conditions:  $u_{N+1} = u_1$

$$u_{N+1} = u_q e^{iq(N+1)2a - i\omega t} = e^{iqN2a} \underbrace{u_q e^{iq2a - i\omega t}}_{u_1} = u_1$$

$$\Rightarrow e^{iqN2a} = 1$$

$$\Rightarrow qN2a = 2\pi\ell, \text{ where } \ell = \text{integer}$$

$$\Rightarrow q = \frac{\pi\ell}{Na}$$

Suppose that  $q$  is restricted to the first Brillouin zone, i.e.,

$$-\frac{\pi}{2a} \leq q < \frac{\pi}{2a} \Rightarrow -\frac{\pi}{2a} \leq \frac{\pi\ell}{Na} < \frac{\pi}{2a} \Rightarrow -\frac{N}{2} \leq \ell < \frac{N}{2}$$

$\Rightarrow$  The total number of  $q$  values in the first Brillouin zone is  $N$ .

$$\text{Since } \Delta q = \frac{\pi}{Na}$$

$\Rightarrow q$  is *discretized*. When  $N$  is taken to infinity (thermodynamic limit),  $\Delta q \rightarrow 0$ , the  $q$  values tend to a continuum.

3. At zone boundaries  $q = \pi/2a$

$$\begin{cases} \omega_2^2(q) = \frac{K}{M_1 M_2} \left( M_1 + M_2 + \sqrt{(M_1 + M_2)^2 - 4M_1 M_2} \right) \\ \omega_1^2(q) = \frac{K}{M_1 M_2} \left( M_1 + M_2 - \sqrt{(M_1 + M_2)^2 - 4M_1 M_2} \right) \end{cases}$$

$$\Rightarrow \begin{cases} \omega_2^2(q) = \frac{K}{M_1 M_2} \left( M_1 + M_2 + \sqrt{(M_1 - M_2)^2} \right) \\ \omega_1^2(q) = \frac{K}{M_1 M_2} \left( M_1 + M_2 - \sqrt{(M_1 - M_2)^2} \right) \end{cases}$$

$$\Rightarrow \begin{cases} \omega_2^2(q) = \frac{K}{M_1 M_2} (M_1 + M_2 + |M_1 - M_2|) \\ \omega_1^2(q) = \frac{K}{M_1 M_2} (M_1 + M_2 - |M_1 - M_2|) \end{cases}$$

Assume  $M_2 > M_1$

$$\omega_2^2(q) = \frac{K}{M_1 M_2} (M_1 + M_2 + (M_2 - M_1)) = \frac{2K}{M_1} \Rightarrow \omega_2 = \sqrt{\frac{2K}{M_1}}$$

$$\omega_1^2(q) = \frac{K}{M_1 M_2} (M_1 + M_2 - (M_2 - M_1)) = \frac{2K}{M_2} \Rightarrow \omega_1 = \sqrt{\frac{2K}{M_2}}$$

$$v_{\text{group}} = \left| \frac{d\omega_{1,2}(q)}{dq} \right|_{q=\pi/2a} = 0$$

$\Rightarrow$  The modes at  $q = \pi/a$  do not transfer energy.

$\Rightarrow$  No energy transfer implies the elastic scattering  $|\vec{k}'| = |\vec{k}|$  of the X-ray.

$\Rightarrow$  Bragg diffraction of the X-ray

4. Near the zone center ( $q \rightarrow 0$ , i.e., long wavelength limit)

$$\omega_2^2(q) \approx \frac{2K(M_1 + M_2)}{M_1 M_2} = \text{constant}$$

$$\omega_1^2(q) \approx \frac{2K}{M_1 + M_2} q^2 a^2 = s^2 q^2$$

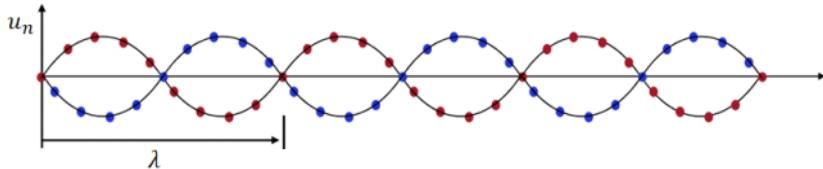
$$v_{\text{group}} = \left| \frac{d\omega_2(q)}{dq} \right|_{q=0} = 0$$

$$v_{\text{group}} = \left| \frac{d\omega_1(q)}{dq} \right|_{q=0} = s$$

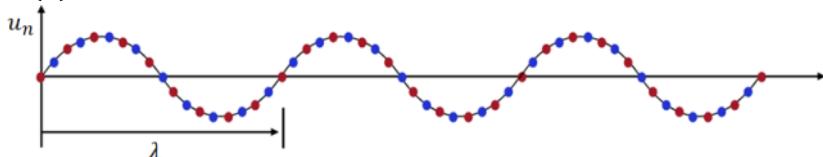
where  $s = \sqrt{\frac{2K}{M_1+M_2}} a$  is the sound velocity.

### (3) Structure of vibrations:

$\omega_2(q)$  band is called the "optical" band.



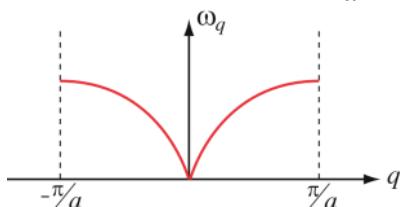
$\omega_1(q)$  band is called the "acoustic" band.



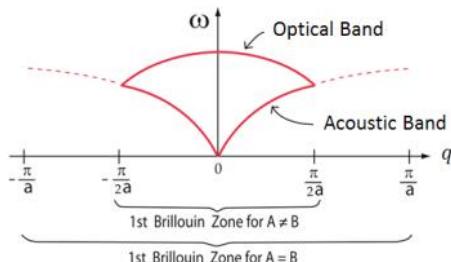
## C. BAND FOLDING

### (1) Physical intuition of energy bands

As the lattice constant =  $a$

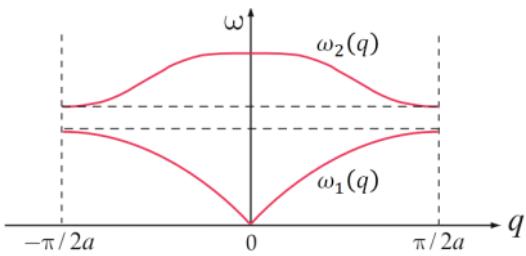


As the lattice constant =  $2a$



The dispersion curve lying outside the region  $|q| \leq \pi/2a$  must be folded back into the first Brillouin zone.

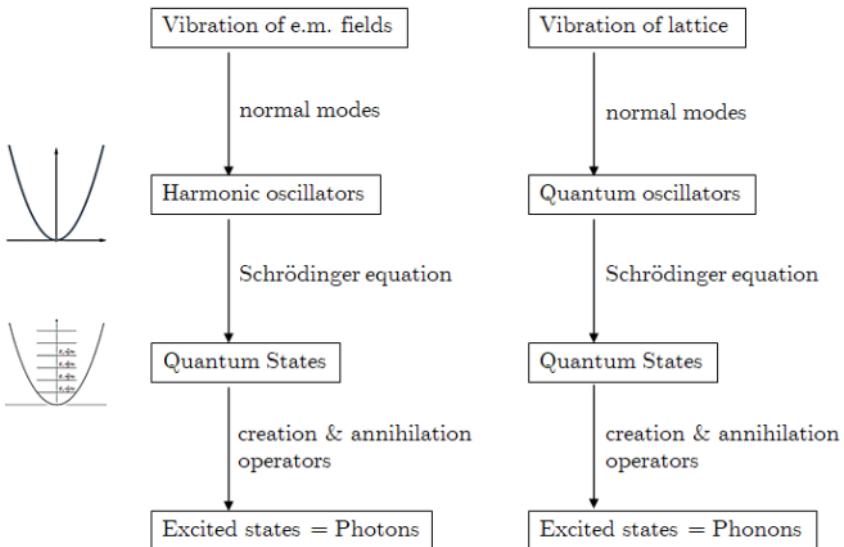
### (2) The band gap opened at the zone boundary due to $M_1 \neq M_2$ .



## 4-2 Particle Properties of Sound

Tuesday, December 20, 2011 8:26 PM

OS:



### A. CLASSICAL LATTICE VIBRATIONS

- (1) Consider  $N$  identical atoms of mass  $M$  with periodic boundary condition. For small displacement on the  $i^{\text{th}}$  atom from its equilibrium position  $\vec{R}_i^0$  one can expand the potential energy near its minimal value

$$\begin{aligned} V(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) &= V(\vec{R}_1^0, \vec{R}_2^0, \dots, \vec{R}_N^0) + \sum_i \left( \frac{\partial V}{\partial \vec{R}_i} \right)_0 (\vec{R}_i - \vec{R}_i^0) \\ &\quad + \frac{1}{2} \sum_{ij} \left( \frac{\partial^2 V}{\partial \vec{R}_i \partial \vec{R}_j} \right)_0 (\vec{R}_i - \vec{R}_i^0)(\vec{R}_j - \vec{R}_j^0) \\ &\quad + \frac{1}{3!} \sum_{ijk} \left( \frac{\partial^3 V}{\partial \vec{R}_i \partial \vec{R}_j \partial \vec{R}_k} \right)_0 (\vec{R}_i - \vec{R}_i^0)(\vec{R}_j - \vec{R}_j^0)(\vec{R}_k - \vec{R}_k^0) + \end{aligned}$$

Let

$$V_0 = V(\vec{R}_1^0, \dots, \vec{R}_N^0)$$

$$\vec{u}_i = \vec{R}_i - \vec{R}_i^0$$

$$V(\vec{R}_1, \dots, \vec{R}_N) = V_0 + \sum_i \left( \frac{\partial V}{\partial \vec{R}_i} \right)_0 \vec{u}_i + \frac{1}{2} \sum_{ij} \left( \frac{\partial^2 V}{\partial \vec{R}_i \partial \vec{R}_j} \right)_0 \vec{u}_i \vec{u}_j \\ + \frac{1}{3!} \sum_{ijk} \left( \frac{\partial^3 V}{\partial \vec{R}_i \partial \vec{R}_j \partial \vec{R}_k} \right)_0 \vec{u}_i \vec{u}_j \vec{u}_k + \dots$$

Since the net force is zero at equilibrium,

$$\left( \frac{\partial V}{\partial \vec{R}_i} \right)_0 = 0$$

Let

$$\vec{D}_{ij} = \left( \frac{\partial^2 V}{\partial \vec{R}_i \partial \vec{R}_j} \right)_0$$

$$\vec{D}_{ijk} = \left( \frac{\partial^3 V}{\partial \vec{R}_i \partial \vec{R}_j \partial \vec{R}_k} \right)_0$$

$$V(\vec{R}_1, \dots, \vec{R}_N) = V_0 + \frac{1}{2} \sum_{ij} \vec{D}_{ij} \vec{u}_i \vec{u}_j + \frac{1}{3!} \sum_{ijk} \vec{D}_{ijk} \vec{u}_i \vec{u}_j \vec{u}_k + \dots$$

- (2) The Hamiltonian of the coupled classical harmonic oscillators

$$\text{Let } V_0 = 0 \text{ and assume } \vec{D}_{ij} = D (\vec{R}_i^0 - \vec{R}_j^0)$$

$$\mathcal{H} = \sum_i \frac{P_i^2}{2M} + V(\vec{R}_1, \dots, \vec{R}_N)$$

$$= \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{ij} D (\vec{R}_i^0 - \vec{R}_j^0) \vec{u}_i \vec{u}_j + \frac{1}{3!} \sum_{ijk} \vec{D}_{ijk} \vec{u}_i \vec{u}_j \vec{u}_k + \dots$$

Up to the second order (harmonic approximation)

$$\mathcal{H} = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{ij} D (\vec{R}_i^0 - \vec{R}_j^0) \vec{u}_i \vec{u}_j$$

It is impossible to solve a set of second-order differential equations.

- (3) Fourier transformations with respect to normal modes  $q$ :

$$\vec{u}_i = \frac{1}{\sqrt{N}} \sum_{q\lambda} Q_{q\lambda} \vec{e}_{q\lambda} e^{i\vec{q}\cdot\vec{R}_i^0}, \quad \lambda = x, y, z$$

$$\vec{P}_i = \frac{1}{\sqrt{N}} \sum_{q\lambda} P_{q\lambda} \vec{e}_{q\lambda} e^{i\vec{q}\cdot\vec{R}_i^0}$$

where  $\vec{e}_{q\lambda}$  is the polarization vector.

The Hamiltonian becomes

$$\begin{aligned}\mathcal{H} = & \frac{1}{N} \sum_i \sum_{\substack{q,q' \\ \lambda,\lambda'}} \frac{P_{q'\lambda'}^* P_{q\lambda}}{2M} \vec{e}_{q'\lambda'} \cdot \vec{e}_{q\lambda} e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0} \\ & + \frac{1}{2N} \sum_{i,j} \sum_{\substack{q,q' \\ \lambda,\lambda'}} Q_{q'\lambda'}^* Q_{q\lambda} \vec{e}_{q'\lambda'} \cdot \vec{e}_{q\lambda} D(\vec{R}_i^0 - \vec{R}_j^0) e^{i\vec{q} \cdot (\vec{R}_j^0 - \vec{R}_i^0)} e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0}\end{aligned}$$

$$\text{Let } \vec{R}_j^0 - \vec{R}_i^0 = \vec{r}$$

$$\begin{aligned}\mathcal{H} = & \frac{1}{N} \sum_i \sum_{\substack{q,q' \\ \lambda,\lambda'}} \frac{P_{q'\lambda'}^* P_{q\lambda}}{2M} \vec{e}_{q'\lambda'} \cdot \vec{e}_{q\lambda} e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0} \\ & + \frac{1}{2N} \sum_{i,r} \sum_{\substack{q,q' \\ \lambda,\lambda'}} Q_{q'\lambda'}^* Q_{q\lambda} \vec{e}_{q'\lambda'} \cdot \vec{e}_{q\lambda} D(\vec{r}) e^{i\vec{q} \cdot \vec{r}} e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0}\end{aligned}$$

$$\text{Let } D(q) = \sum_r D(\vec{r}) e^{i\vec{q} \cdot \vec{r}}$$

$$\begin{aligned}\mathcal{H} = & \frac{1}{N} \sum_i \sum_{\substack{q,q' \\ \lambda,\lambda'}} \frac{P_{q'\lambda'}^* P_{q\lambda}}{2M} \vec{e}_{q'\lambda'} \cdot \vec{e}_{q\lambda} e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0} \\ & + \frac{1}{2N} \sum_i \sum_{\substack{q,q' \\ \lambda,\lambda'}} D(q) Q_{q'\lambda'}^* Q_{q\lambda} \vec{e}_{q'\lambda'} \cdot \vec{e}_{q\lambda} e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0}\end{aligned}$$

$$\text{Since } \sum_i e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_i^0} = N \delta_{\vec{q},\vec{q}'}$$

$$\begin{aligned}\mathcal{H} = & \frac{1}{N} \sum_{\substack{q,q' \\ \lambda,\lambda'}} \frac{P_{q'\lambda'}^* P_{q\lambda}}{2M} \vec{e}_{q\lambda} \cdot \vec{e}_{q\lambda} N \delta_{\vec{q},\vec{q}'} + \frac{1}{2N} \sum_{\substack{q,q' \\ \lambda,\lambda'}} D(q) Q_{q'\lambda'}^* Q_{q\lambda} \vec{e}_{q\lambda} \cdot \vec{e}_{q\lambda} N \delta_{\vec{q},\vec{q}'} \\ = & \sum_q \frac{P_{q\lambda'}^* P_{q\lambda}}{2M} \delta_{\lambda,\lambda'} + \frac{1}{2} \sum_q D(q) Q_{q\lambda'}^* Q_{q\lambda} \delta_{\lambda,\lambda'} \\ = & \sum_{q,\lambda} \frac{P_{q\lambda}^2}{2M} + \frac{1}{2} \sum_{q,\lambda} D(q) Q_{q\lambda}^2 \\ = & \sum_{q,\lambda} \frac{P_{q\lambda}^2}{2M} + \frac{M}{2} \sum_{q,\lambda} \omega_{q\lambda}^2 Q_{q\lambda}^2, \text{ where } \omega_{q\lambda}^2 = \frac{D(q)}{M}\end{aligned}$$

⇒ The Hamiltonian is decoupled into  $N$  independent harmonic oscillators with normal modes  $q$ .

EXAMPLES:

One-atom linear chain with nearest neighbor interactions

$$D(\vec{r}) = Kc_r$$

$$D(q) = K \sum_r c_r e^{i\vec{q} \cdot \vec{r}} = K(c_{-1} e^{-iqa} + c_0 + c_1 e^{iqa})$$

$$\text{Since } D(0) = 0 \text{ and } c_{-1} = c_1 \Rightarrow c_{-1} = c_1 = -\frac{1}{2}c_0$$

$$\text{Let } c_0 = 2 \Rightarrow c_{-1} = c_1 = -1$$

$$D(q) = K(2 - e^{-iqa} - c_1 e^{iqa}) = 2K(1 - \cos qa)$$

$$\omega_{q\lambda} = \sqrt{\frac{D(q)}{M}} = \sqrt{\frac{2K}{M} 2 \sin^2 \frac{qa}{2}} = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{qa}{2} \right|$$

## B. QUANTUM LATTICE VIBRATIONS

(1) Introducing the effect of quantum mechanics:

$$Q_{q\lambda} \rightarrow \hat{Q}_{q\lambda}$$

$$P_{q\lambda} \rightarrow \hat{P}_{q\lambda}$$

$$[\hat{Q}_{q\lambda}, \hat{P}_{q\lambda}] = i\hbar$$

The Hamiltonian operator is

$$\hat{\mathcal{H}} = \sum_{q\lambda} \left( \frac{\hat{P}_{q\lambda}^2}{2M} + \frac{M}{2} \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 \right)$$

⇒ The crystal lattice vibrations are described as a sum of  $N$  independent quantum harmonic oscillators.

The Schrödinger equation of a harmonic oscillator:

$$\left( \frac{\hat{P}_{q\lambda}^2}{2M} + \frac{M}{2} \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 \right) \psi_n = \hbar \omega_{q\lambda} \left( n_{q\lambda} + \frac{1}{2} \right) \psi_n$$

$$\Rightarrow \frac{1}{\hbar \omega_{q\lambda}} \left( \frac{\hat{P}_{q\lambda}^2}{2M} + \frac{M}{2} \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 \right) \psi_n = \left( n_{q\lambda} + \frac{1}{2} \right) \psi_n$$

$$\Rightarrow \left[ \frac{1}{\hbar \omega_{q\lambda}} \left( \frac{\hat{P}_{q\lambda}^2}{2M} + \frac{M}{2} \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 \right) - \frac{1}{2} \right] \psi_n = n_{q\lambda} \psi_n$$

Define an operator  $\hat{n}_{q\lambda}$  such that  $\hat{n}_{q\lambda} \psi_n(q, \lambda) = n_{q\lambda} \psi_n(q, \lambda)$ ,

$$\hat{n}_{q\lambda} = \frac{1}{\hbar\omega_{q\lambda}} \left( \frac{\hat{P}_{q\lambda}^2}{2M} + \frac{M}{2} \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 \right) - \frac{1}{2}$$

$\Rightarrow$  The eigenvalues of the operator  $\hat{n}_{q\lambda}$  are the integers  $n_{q\lambda}$  and  $\hat{n}_{q\lambda}$  is called the number operator.

$$\hat{\mathcal{H}} = \sum_{q\lambda} \hbar\omega_{q\lambda} \left( \hat{n}_{q\lambda} + \frac{1}{2} \right)$$

- (2) Introducing the creation and annihilation operators:

Let the position and momentum operators as

$$\hat{Q}_{q\lambda} = \sqrt{\frac{\hbar}{2M\omega_{q\lambda}}} (\hat{a}_{q\lambda} + \hat{a}_{-q\lambda}^\dagger)$$

$$\hat{P}_{q\lambda} = i \sqrt{\frac{M\hbar\omega_{q\lambda}}{2}} (\hat{a}_{-q\lambda}^\dagger - \hat{a}_{q\lambda})$$

The inverse relations are

$$\hat{a}_{q\lambda} = \frac{1}{\sqrt{2M\hbar\omega_{q\lambda}}} (M\omega_{q\lambda} \hat{Q}_{q\lambda} + i\hat{P}_{q\lambda})$$

$$\hat{a}_{q\lambda}^\dagger = \frac{1}{\sqrt{2M\hbar\omega_{q\lambda}}} (M\omega_{q\lambda} \hat{Q}_{q\lambda} - i\hat{P}_{q\lambda})$$

Since  $\hat{a}_{q\lambda} \neq \hat{a}_{q\lambda}^\dagger$ ,  $\hat{a}_{q\lambda}$  and  $\hat{a}_{q\lambda}^\dagger$  are nonhermitian operators, we consider the product of  $\hat{a}_{q\lambda}$  and  $\hat{a}_{q\lambda}^\dagger$ , such that  $(\hat{a}_{q\lambda}^\dagger \hat{a}_{q\lambda})^\dagger = \hat{a}_{q\lambda}^\dagger \hat{a}_{q\lambda}$  is a hermitian operator,

$$\begin{aligned} \hat{a}_{q\lambda}^\dagger \hat{a}_{q\lambda} &= \frac{1}{2M\hbar\omega_{q\lambda}} (M\omega_{q\lambda} \hat{Q}_{q\lambda} - i\hat{P}_{q\lambda})(M\omega_{q\lambda} \hat{Q}_{q\lambda} + i\hat{P}_{q\lambda}) \\ &= \frac{1}{2M\hbar\omega_{q\lambda}} \left( \hat{P}_{q\lambda}^2 + M^2 \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 + iM\omega_{q\lambda} (\hat{Q}_{q\lambda} \hat{P}_{q\lambda} - \hat{P}_{q\lambda} \hat{Q}_{q\lambda}) \right) \\ &= \frac{1}{\hbar\omega_{q\lambda}} \left( \frac{\hat{P}_{q\lambda}^2}{2M} + \frac{M}{2} \omega_{q\lambda}^2 \hat{Q}_{q\lambda}^2 \right) - \frac{1}{2} \\ &= \hat{n}_{q\lambda} \end{aligned}$$

$$\hat{\mathcal{H}} = \sum_{q\lambda} \hbar\omega_{q\lambda} \left( \hat{n}_{q\lambda} + \frac{1}{2} \right) = \sum_{q\lambda} \hbar\omega_{q\lambda} \left( \hat{a}_{q\lambda}^\dagger \hat{a}_{q\lambda} + \frac{1}{2} \right)$$

The commutation relation between  $\hat{a}_{q\lambda}$  and  $\hat{a}_{q\lambda}^\dagger$

$$\begin{aligned}
[\hat{a}_{q\lambda}, \hat{a}_{q\lambda}^\dagger] &= \frac{1}{2m\hbar\omega_{q\lambda}} [(m\omega_{q\lambda}\hat{Q}_{q\lambda} + i\hat{P}_{q\lambda}), (m\omega_{q\lambda}\hat{Q}_{q\lambda} - i\hat{P}_{q\lambda})] \\
&= \frac{1}{2m\hbar\omega_{q\lambda}} ([i\hat{P}_{q\lambda}, m\omega_{q\lambda}\hat{Q}_{q\lambda}] + [m\omega_{q\lambda}\hat{Q}_{q\lambda}, -i\hat{P}_{q\lambda}]) \\
&= \frac{i}{2\hbar} [\hat{P}_{q\lambda}, \hat{Q}_{q\lambda}] - \frac{i}{2\hbar} [\hat{Q}_{q\lambda}, \hat{P}_{q\lambda}] \\
&= \frac{i}{2\hbar} (-i\hbar) - \frac{i}{2\hbar} (i\hbar) \\
&= 1
\end{aligned}$$

$$\Rightarrow \hat{a}_{q\lambda}\hat{a}_{q\lambda}^\dagger = \hat{a}_{q\lambda}^\dagger\hat{a}_{q\lambda} + 1$$

Thus, we can show that

$$\hat{a}_{q\lambda}\psi_n = \sqrt{n}\psi_{n-1}$$

$$\hat{a}_{q\lambda}^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}$$

The excited states:

Let  $\psi_0$  be the ground state, and  $\hat{a}\psi_0 \equiv 0$

$$\psi_n = \frac{\hat{a}_{q\lambda}^\dagger}{\sqrt{n}}\psi_{n-1} = \frac{\hat{a}_{q\lambda}^\dagger}{\sqrt{n}} \cdots \frac{\hat{a}_{q\lambda}^\dagger}{\sqrt{1}}\psi_0 = \frac{(\hat{a}_{q\lambda}^\dagger)^n}{\sqrt{n!}}\psi_0$$

Here,  $\psi_n$  is obtained by applying  $\hat{a}_{q\lambda}^\dagger$  to the ground state  $n$  times and the associated energy is

$$\varepsilon_n = \hbar\omega_{q\lambda} \left( n_{q\lambda} + \frac{1}{2} \right)$$

Define a quantum (transition between energy levels) with energy

$$\Delta\varepsilon = \varepsilon_n(q, \lambda) - \varepsilon_{n-1}(q, \lambda)$$

$$\begin{aligned}
&= \hbar\omega_{q\lambda} \left( n_{q\lambda} + \frac{1}{2} \right) - \hbar\omega_{q\lambda} \left( (n_{q\lambda} - 1) + \frac{1}{2} \right) \\
&= \hbar\omega_{q\lambda}
\end{aligned}$$

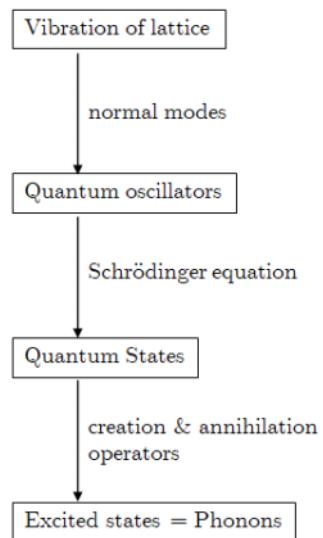
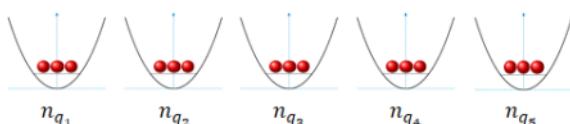
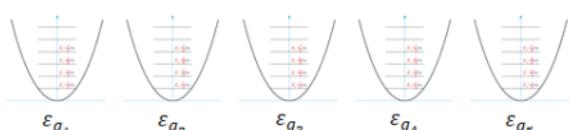
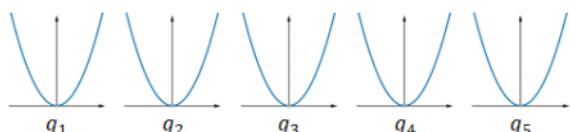
The excited states are referred to as particles, called **phonons**.

$$\frac{\varepsilon_n}{\Delta\varepsilon} - \frac{\varepsilon_0}{\Delta\varepsilon} = \left( n_{q\lambda} + \frac{1}{2} \right) - \frac{1}{2} = n_{q\lambda}$$

Thus,  $\hat{a}_{q\lambda}^\dagger$  is called the creation operator and  $\hat{a}_{q\lambda}$  is called the annihilation operator.



all atoms move with the same frequency



## EXAMPLES:

The canonical partition function of an oscillator is

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\hbar\omega(n+1/2)/k_B T} \\ &= e^{-\hbar\omega/2k_B T} \sum_n e^{-n\hbar\omega/k_B T} \\ &= \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} \end{aligned}$$

$$\ln Z = -\ln(1 - e^{-\hbar\omega/k_B T}) - \frac{\hbar\omega}{2k_B T}$$

The mean energy of one oscillator is

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{\hbar\omega e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}} + \frac{\hbar\omega}{2} \\ &= \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} + \frac{\hbar\omega}{2} \\ &= \hbar\omega \left( \langle n \rangle + \frac{1}{2} \right) \end{aligned}$$

where

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

is the Bose-Einstein distribution function.

### C. PHONON-PHONON INTERACTIONS

- (1) Fourier transformation of the 3rd-order term, i.e., anharmonic term:

$$\mathcal{H}' = \frac{1}{3!} \sum_{ijk} \vec{D}_{ijk} \vec{u}_i \vec{u}_j \vec{u}_k$$

$$\text{Let } \vec{u}_i = \frac{1}{\sqrt{N}} \sum_{q\lambda} Q_{q\lambda} \vec{e}_{q\lambda} e^{i\vec{q}\cdot\vec{R}_i^0}, \quad \lambda = x, y, z$$

$$\mathcal{H}' = \frac{1}{3!} \left( \frac{1}{N} \right)^{3/2} \sum_{ijk} \sum_{qq'q''} \vec{D}_{ijk} Q_{q\lambda} Q_{q'\lambda} Q_{q''\lambda} e^{i\vec{q}\cdot\vec{R}_i^0} e^{i\vec{q}'\cdot\vec{R}_j^0} e^{i\vec{q}''\cdot\vec{R}_k^0}$$

$$\text{Let } \vec{R}_j^0 = \vec{R}_i^0 + \vec{r}' \text{ and } \vec{R}_k^0 = \vec{R}_i^0 + \vec{r}''$$

$$\sum_{ijk} \vec{D}_{ijk} e^{i\vec{q}\cdot\vec{R}_i^0} e^{i\vec{q}'\cdot\vec{R}_j^0} e^{i\vec{q}''\cdot\vec{R}_k^0}$$

$$= \sum_{r', r''} D(\vec{r}', \vec{r}'') e^{i\vec{q}\cdot\vec{R}_i^0} e^{i\vec{q}'\cdot(\vec{R}_i^0 + \vec{r}')} e^{i\vec{q}''\cdot(\vec{R}_k^0 + \vec{r}'')}$$

$$= \sum_{r', r''} D(\vec{r}', \vec{r}'') e^{i\vec{q}'\cdot\vec{r}'} e^{i\vec{q}''\cdot\vec{r}''} \sum_i e^{i(\vec{q} + \vec{q}' + \vec{q}'')\cdot\vec{R}_i^0}$$

$$= \sum_{r', r''} D(\vec{r}', \vec{r}'') e^{i\vec{q}'\cdot\vec{r}'} e^{i\vec{q}''\cdot\vec{r}''} N\delta(\vec{q} + \vec{q}' + \vec{q}'')$$

Define

$$D(\vec{q}', \vec{q}'') = \frac{1}{\sqrt{N}} \sum_{r', r''} D(\vec{r}', \vec{r}'') e^{i\vec{q}'\cdot\vec{r}'} e^{i\vec{q}''\cdot\vec{r}''}$$

The Hamiltonian becomes

$$\begin{aligned} \mathcal{H}' &= \frac{1}{3!} \frac{1}{N} \sum_{qq'q''} D(\vec{q}', \vec{q}'') Q_{q\lambda} Q_{q'\lambda} Q_{q''\lambda} N\delta(\vec{q} + \vec{q}' + \vec{q}'') \\ &= \frac{1}{3!} \sum_{qq'} D(\vec{q}, \vec{q}') Q_{q\lambda} Q_{q'\lambda} Q_{-(q+q')\lambda} \end{aligned}$$

- (2) Introducing the creation and annihilation operators, the Hamiltonian  $\hat{\mathcal{H}'}$  becomes

$$\hat{H}' = \frac{1}{3!} \sum_{qq'} D(\vec{q}, \vec{q}') \left( \hat{a}_{q\lambda} + \hat{a}_{-q\lambda}^\dagger \right) \left( \hat{a}_{q'\lambda} + \hat{a}_{-q'\lambda}^\dagger \right) \left( \hat{a}_{-(q+q')\lambda} + \hat{a}_{(q+q')\lambda}^\dagger \right)$$

The Hamiltonian can be expanded to eight terms.

$$\hat{a}_{q\lambda} \hat{a}_{q'\lambda} \hat{a}_{-(q+q')\lambda} \dots \text{(a)}$$

$$\hat{a}_{q\lambda} \hat{a}_{q'\lambda} \hat{a}_{(q+q')\lambda}^\dagger \dots \text{(b)}$$

$$\hat{a}_{q\lambda} \hat{a}_{-q'\lambda}^\dagger \hat{a}_{-(q+q')\lambda} \dots \text{(b)}$$

$$\hat{a}_{-q\lambda}^\dagger \hat{a}_{q'\lambda} \hat{a}_{-(q+q')\lambda} \dots \text{(b)}$$

$$\hat{a}_{q\lambda} \hat{a}_{-q'\lambda}^\dagger \hat{a}_{(q+q')\lambda}^\dagger \dots \text{(c)}$$

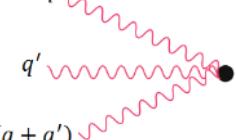
$$\hat{a}_{-q\lambda}^\dagger \hat{a}_{q'\lambda} \hat{a}_{(q+q')\lambda}^\dagger \dots \text{(c)}$$

$$\hat{a}_{-q\lambda}^\dagger \hat{a}_{-q'\lambda}^\dagger \hat{a}_{-(q+q')\lambda} \dots \text{(c)}$$

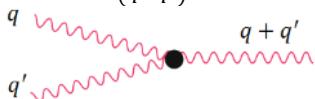
$$\hat{a}_{-q\lambda}^\dagger \hat{a}_{-q'\lambda}^\dagger \hat{a}_{(q+q')\lambda}^\dagger \dots \text{(d)}$$

(3) There are four different scattering processes.

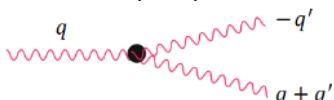
1.  $\hat{a}_{q\lambda} \hat{a}_{q'\lambda} \hat{a}_{-(q+q')\lambda}$ : annihilates three phonons



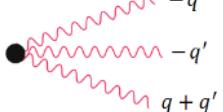
2.  $\hat{a}_{q\lambda} \hat{a}_{q'\lambda} \hat{a}_{(q+q')\lambda}^\dagger$ : annihilates two phonons and creates one phonon



3.  $\hat{a}_{q\lambda} \hat{a}_{-q'\lambda}^\dagger \hat{a}_{(q+q')\lambda}^\dagger$ : annihilates a phonon and creates two phonons



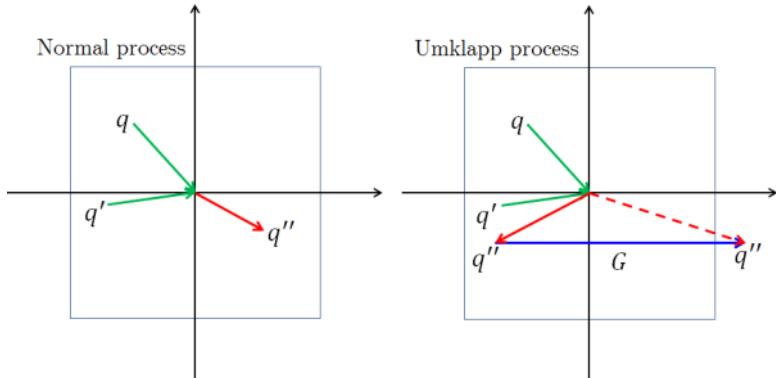
4.  $\hat{a}_{-q\lambda}^\dagger \hat{a}_{-q'\lambda}^\dagger \hat{a}_{(q+q')\lambda}^\dagger$ : creates three phonons



Most phonon-phonon scattering are processes (b) and (c)



(4) Normal process and umklapp process



Umkapp process (backscattering process):  $q$ -values are close to  $\vec{G}$  and the sum of  $\vec{q}$  and  $\vec{q}'$  is outside the first Brillouin zone.

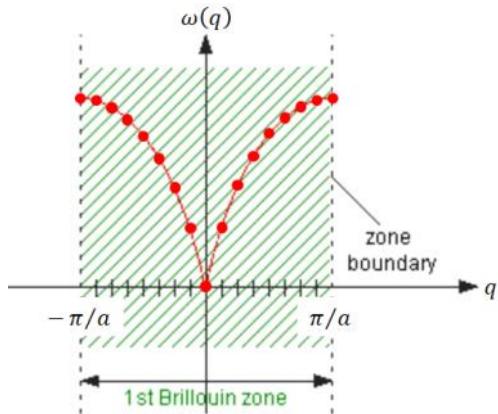
$$\vec{q}'' = \vec{q} + \vec{q}' - \vec{G}$$

## 4-3 Density of States of Phonons

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### A. BAND STRUCTURES OF PHONONS

- (1) Band structure of phonons characterizes the modes of vibrations of lattice.



- (2) The number of phonons  $dn$  allows us to know the thermal properties of a crystal. Since  $dn = g(\omega)d\omega$ , thus, knowing the density of states  $g(\omega)$  is an important understanding of the properties of a crystal.

### B. DENSITY OF STATES OF PHONONS

- (1) One-atom linear chain with nearest-neighbor interactions  
The dispersion relation is

$$\omega(q) = \frac{\gamma}{\sqrt{2}}(1 - \cos qa)^{1/2} = \gamma \left| \sin \frac{qa}{2} \right|, \text{ where } \gamma = 2 \sqrt{\frac{K}{M}}$$

1. Direct integral approach:

$$g(\omega) = \frac{1}{2\pi} \int \delta(\omega_q - \omega) dq$$

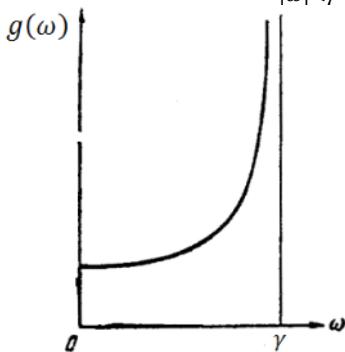
Since  $\omega_q$  is an even function,  $\delta(\omega_q^2 - \omega^2) = \frac{1}{2} \left[ \frac{\delta(\omega_q - \omega)}{\omega} + \frac{\delta(\omega_q + \omega)}{\omega} \right]$

$$\begin{aligned}
g(\omega) &= \frac{2\omega}{2\pi} \int \delta(\omega_q^2 - \omega^2) dq \\
&= \frac{2\omega}{2\pi} \int \int_{-\infty}^{\infty} e^{-i\alpha(\omega_q^2 - \omega^2)} \frac{d\alpha}{2\pi} dq \\
&= \frac{2\omega}{2\pi} \int \int_{-\infty}^{\infty} e^{i\alpha \left[ \omega^2 - \frac{\gamma^2}{2}(1 - \cos qa) \right]} \frac{d\alpha}{2\pi} dq \\
&= 2\omega \int_{-\infty}^{\infty} e^{i\alpha \left( \omega^2 - \frac{\gamma^2}{2} \right)} \frac{d\alpha}{2\pi} \cdot \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i\alpha \frac{\gamma^2}{2} \cos qa} dq
\end{aligned}$$

$$= \frac{2\omega}{a} \int_{-\infty}^{\infty} e^{i\alpha \left( \omega^2 - \frac{\gamma^2}{2} \right)} J_0 \left( \frac{\gamma^2}{2} \alpha \right) \frac{d\alpha}{2\pi}$$

Let  $x = \frac{\gamma^2}{2}\alpha$  and  $k = \frac{2}{\gamma^2} \left( \omega^2 - \frac{\gamma^2}{2} \right)$

$$\begin{aligned}
g(\omega) &= \frac{2\omega}{a} \frac{1}{2\pi} \frac{2}{\gamma^2} \int_{-\infty}^{\infty} J_0(x) e^{ikx} dx \dots \text{Fourier transform} \\
&= \frac{2\omega}{a} \frac{1}{2\pi} \frac{2}{\gamma^2} \left[ 2 \frac{\Theta(k+1) - \Theta(k-1)}{\sqrt{1-k^2}} \right] \\
&= \frac{2}{\pi a} \frac{1}{\gamma} \frac{2\omega}{\gamma} \left[ \frac{1}{\sqrt{1-k^2}} \right]_{-1 < k < 1} \\
&= \frac{2}{\pi a} \frac{1}{\sqrt{\gamma^2 - \omega^2}} \Big|_{|\omega| < \gamma}
\end{aligned}$$



2. Surface integral approach:

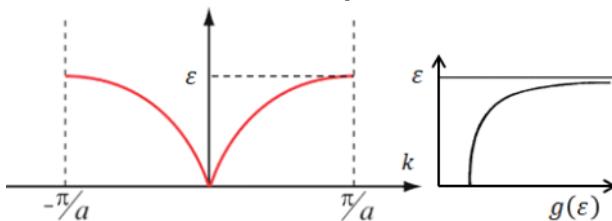
Since  $\omega_q$  is isotropic

$$g(\omega) = \frac{1}{2\pi} \int \frac{dS}{|\nabla_q \omega_q|} = \frac{1}{2\pi} \frac{2}{|d\omega/dq|} = \frac{1}{\pi} \frac{1}{|d\omega/dq|}$$

$$\text{Since } \left| \frac{d\omega}{dq} \right| = \gamma \left| \frac{d}{dq} \sin \frac{qa}{2} \right| = \frac{\gamma a}{2} \cos \frac{qa}{2}$$

$$g(\omega) = \frac{1}{\pi} \frac{1}{\frac{\gamma a}{2} \cos \frac{qa}{2}} = \frac{2}{\pi a} \frac{1}{\gamma \sqrt{1 - \omega^2/\gamma^2}} = \frac{2}{\pi a} \frac{1}{\sqrt{\gamma^2 - \omega^2}}$$

### 3. Band structure and density of states



#### (2) One-atom square lattice with nearest-neighbor interactions

The dispersion relation is

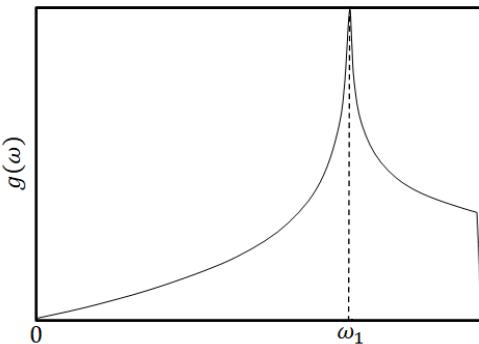
$$\omega(q) = \frac{\gamma}{2} \left( 2 - \cos q_x a - \cos q_y a \right)^{1/2}$$

##### 1. Direct integral approach:

$$\begin{aligned} g(\omega) &= \frac{1}{(2\pi)^2} \int \delta(\omega_q - \omega) d^2q \\ &= \frac{2\omega}{(2\pi)^2} \int \delta(\omega_q^2 - \omega^2) d^2q \\ &= \frac{2\omega}{(2\pi)^2} \int \int_{-\infty}^{\infty} e^{-i\alpha(\omega_q^2 - \omega^2)} \frac{d\alpha}{2\pi} d^2q \\ &= \frac{2\omega}{(2\pi)^2} \int \int_{-\infty}^{\infty} e^{i\alpha \left[ \omega^2 - \frac{\gamma^2}{4}(2 - \cos q_x a - \cos q_y a) \right]} \frac{d\alpha}{2\pi} d^2q \\ &= \frac{2\omega}{a^2} \int_{-\infty}^{\infty} e^{i\alpha \left( \omega^2 - \frac{\gamma^2}{2} \right)} J_0^2 \left( \frac{\gamma^2}{4} \alpha \right) \frac{d\alpha}{2\pi} \end{aligned}$$

$$\text{Let } x = \frac{\gamma^2}{4} \alpha \text{ and } k = \frac{4}{\gamma^2} \left( \omega^2 - \frac{\gamma^2}{2} \right)$$

$$g(\omega) = \frac{2\omega}{a^2} \frac{1}{2\pi} \frac{4}{\gamma^2} \int_{-\infty}^{\infty} J_0^2(x) e^{ikx} dx \xrightarrow{?} \frac{2}{\pi a^2} \frac{2\omega}{\gamma^2} \frac{1}{\pi} K \left[ \frac{2\omega}{\gamma} \left( 1 - \frac{\omega^2}{\gamma^2} \right) \right]$$



The singularities occur as  $|\nabla_q \omega_q| = 0$ ,

$$\begin{aligned}\nabla_q \omega_q &= \frac{\gamma}{2} \frac{a(\sin q_x a + \sin q_y a)}{\sqrt{2 - \cos q_x a - \cos q_y a}} = 0 \\ \Rightarrow \vec{q} &= \left(\frac{\pi}{2a}, -\frac{\pi}{2a}\right) \Rightarrow \omega_1 = \frac{\gamma}{2} \sqrt{2}\end{aligned}$$

- (3) One-atom cubic lattice with nearest-neighbor interactions

The dispersion relation is

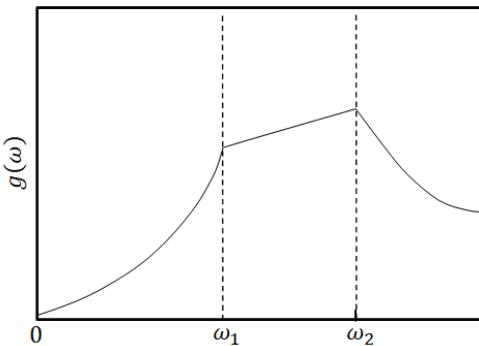
$$\omega(q) = \frac{\gamma}{\sqrt{6}} \left( 3 - \cos q_x a - \cos q_y a - \cos q_z a \right)^{1/2}$$

1. Direct integral approach:

$$\begin{aligned}g(\omega) &= \frac{1}{(2\pi)^3} \int \delta(\omega_q - \omega) d^3 q \\ &= \frac{2\omega}{(2\pi)^3} \int \delta(\omega_q^2 - \omega^2) d^3 q \\ &= \frac{2\omega}{(2\pi)^3} \int \int_{-\infty}^{\infty} e^{-i\alpha(\omega_q^2 - \omega^2)} \frac{d\alpha}{2\pi} d^3 q \\ &= \frac{2\omega}{(2\pi)^3} \int \int_{-\infty}^{\infty} e^{i\alpha \left[ \omega^2 - \frac{\gamma^2}{6}(3 - \cos q_x a - \cos q_y a - \cos q_z a) \right]} \frac{d\alpha}{2\pi} d^3 q \\ &= \frac{2\omega}{a^3} \int_{-\infty}^{\infty} e^{i\alpha \left( \omega^2 - \frac{\gamma^2}{2} \right)} J_0^3 \left( \frac{\gamma^2}{6} \alpha \right) \frac{d\alpha}{2\pi}\end{aligned}$$

$$\text{Let } x = \frac{\gamma^2}{6} \alpha \text{ and } k = \frac{6}{\gamma^2} \left( \omega^2 - \frac{\gamma^2}{2} \right)$$

$$g(\omega) = \frac{2\omega}{a^3} \frac{1}{2\pi} \frac{6}{\gamma^2} \int_{-\infty}^{\infty} J_0^3(x) e^{ikx} dx$$



The singularities occur as  $|\nabla_q \omega_q| = 0$ ,

$$\nabla_q \omega_q = \frac{\gamma}{\sqrt{6}} \frac{a(\sin q_x a + \sin q_y a + \sin q_z a)}{\sqrt{3 - \cos q_x a - \cos q_y a - \cos q_z a}} = 0$$

$$\vec{q} = \left( \frac{\pi}{2a}, -\frac{\pi}{2a}, 0 \right) \Rightarrow \omega_1 = \frac{1}{\sqrt{3}}\gamma$$

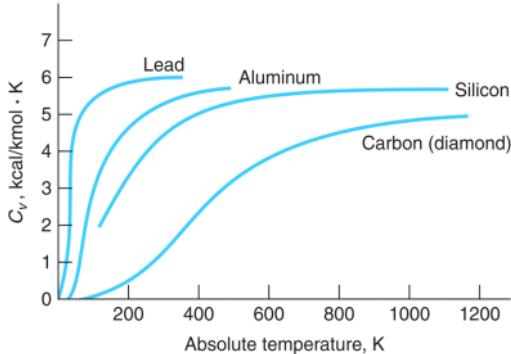
$$\vec{q} = \left( \frac{\pi}{2a}, -\frac{\pi}{2a}, \pm \frac{\pi}{a} \right) \Rightarrow \omega_2 = \sqrt{\frac{2}{3}}\gamma$$

## 4-4 Thermal Properties of Phonons

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### A. DULONG-PETIT LAW (1819)

- (1) The empirical Dulong-Petit law  $C_V = 3R$



- (2) Classical model

Equipartition theorem

$$\varepsilon_{q\lambda} = k_B T$$

Density of states

$$g(\varepsilon) = \frac{1}{V}$$

Internal energy

$$U = \sum_{q\lambda} \varepsilon_{q\lambda} \langle n \rangle = 3k_B T \sum_q \frac{N e^{-\varepsilon_q / k_B T}}{Z} = 3k_B T V \int_0^\infty \frac{N e^{-\varepsilon / k_B T}}{Z} g(\varepsilon) d\varepsilon$$

$$\text{Since } Z = \sum_q e^{-\varepsilon_q / k_B T} = V \int e^{-\varepsilon / k_B T} g(\varepsilon) d\varepsilon = V \int_0^\infty \frac{e^{-\varepsilon / k_B T}}{V} d\varepsilon = k_B T$$

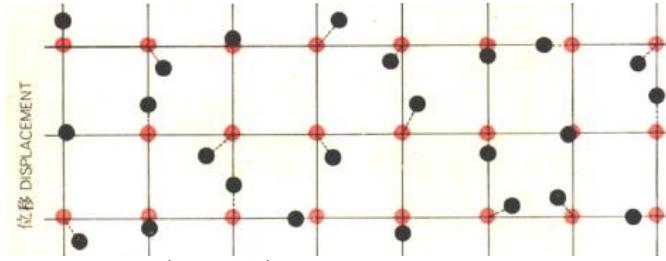
$$U = 3Nk_B T V \int_0^\infty \frac{e^{-\varepsilon / k_B T}}{k_B T} \frac{1}{V} d\varepsilon = 3N \int_0^\infty e^{-\varepsilon / k_B T} d\varepsilon = 3Nk_B T$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 3Nk_B = 3R$$

### B. EINSTEIN MODEL (1907)

- (1) Einstein assume:

- The motion of each atom is described by an independent harmonic oscillator



$$\varepsilon_{q\lambda} = \hbar\omega_{q\lambda} \left( n_{q\lambda} + \frac{1}{2} \right)$$

- Each atom vibrates with the same frequency  $\omega_E$ .

$$\omega_{q\lambda} = \omega_E$$

(2) Internal energy (in thermal equilibrium)

$$\begin{aligned} U &= \sum_{q\lambda} \hbar\omega_{q\lambda} \left( \langle n_{q\lambda} \rangle + \frac{1}{2} \right) \\ &= 3 \sum_q \hbar\omega_q \left( \langle n_q \rangle + \frac{1}{2} \right) \\ &= 3V \int \hbar\omega \left( \langle n \rangle + \frac{1}{2} \right) g(\omega) d\omega \end{aligned}$$

Here,

The Bose-Einstein distribution determines the equilibrium number of phonons with a given frequency.

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

The density of states

$$g(\omega) = \frac{1}{(2\pi)^3} \int \delta(\omega - \omega_{q\lambda}) d^3 q = \delta(\omega - \omega_E) \int \frac{d^3 q}{(2\pi)^3}$$

$$\text{Since } N = \sum_{q \in \text{BZ}} 1 = V \int \frac{d^3 q}{(2\pi)^3}$$

$$\Rightarrow g(\omega) = \delta(\omega - \omega_E) \frac{N}{V}$$

Thus, we obtain

$$\begin{aligned}
U &= 3\mathcal{V} \int_0^\infty \left( \frac{\hbar\omega_E}{e^{\hbar\omega/k_B T} - 1} + \frac{\hbar\omega_E}{2} \right) \delta(\omega - \omega_E) \frac{N}{\mathcal{V}} d\omega \\
&= 3N \int_0^\infty \frac{\hbar\omega_E}{e^{\hbar\omega/k_B T} - 1} \delta(\omega - \omega_E) d\omega + 3N \frac{\hbar\omega_E}{2} \\
&= \frac{3N\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1} + \frac{3N\hbar\omega_E}{2} \\
C_V &= \left( \frac{\partial U}{\partial T} \right)_V = 3Nk_B \left( \frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{\hbar\omega_E/k_B T}}{(e^{\hbar\omega_E/k_B T} - 1)^2}
\end{aligned}$$

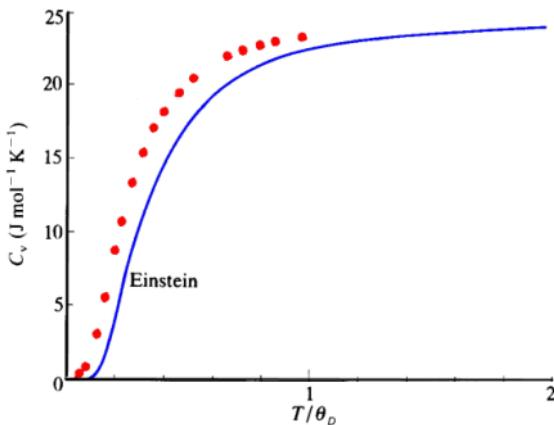
Alternative method: (using partition function)

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_E(n+\frac{1}{2})} = e^{-\beta\hbar\omega_E/2} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_E} = e^{-\beta\hbar\omega_E/2} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_E})^n$$

$$\text{Since } \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$Z = \frac{e^{-\beta\hbar\omega_E/2}}{1 - e^{-\beta\hbar\omega_E}} = \frac{1}{e^{\beta\hbar\omega_E/2} - e^{-\beta\hbar\omega_E/2}} = \frac{1}{2 \sinh\left(\frac{\beta\hbar\omega_E}{2}\right)}$$

$$C_V = 3N \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2} = 3Nk_B \left( \frac{\hbar\omega_E}{k_B T} \right)^2 \frac{1}{\sinh^2\left(\frac{\hbar\omega_E}{2k_B T}\right)}$$



(3) Limit

$$\text{Let } x = \frac{\hbar\omega_E}{k_B T}$$

$$C_V = 3Nk_B \frac{x^2 e^x}{(e^x - 1)^2} = 3Nk_B \frac{x^2}{e^x - 2 + e^{-x}} = 3Nk_B \frac{x^2}{(e^x - 1)(1 - e^{-x})}$$

1. Low-temperature limit:  $k_B T \ll \hbar\omega_E \Rightarrow x \gg 1$

$$e^x - 1 \approx e^x$$

$$1 - e^{-x} \approx 1$$

$$C_V \approx 3R \frac{x^2}{e^x} = 3R \left( \frac{\hbar\omega_E}{k_B T} \right)^2 e^{-\hbar\omega_E/k_B T} \propto \frac{e^{-\hbar\omega_E/k_B T}}{T^2}$$

2. High-temperature limit:  $k_B T \gg \hbar\omega_E \Rightarrow x \ll 1$

$$e^x - 1 = (1 + x + \dots) - 1 \approx x$$

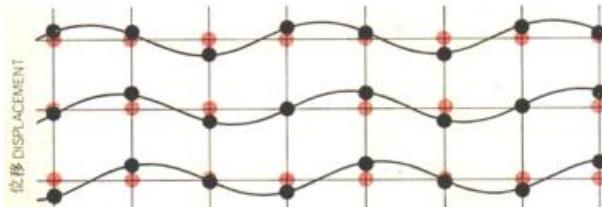
$$1 - e^{-x} = 1 - (1 - x + \dots) \approx x$$

$$C_V \approx 3Nk_B \frac{x^2}{x \cdot x} = 3R$$

### C. DEBYE MODEL (1912)

(1) Debye assume:

1. Atoms vibrate collectively in a wave-like fashion.



2. All atoms move with the same frequency called normal modes,

$$\omega_{q\lambda} = v_\lambda q$$

(2) Internal energy

$$U = \sum_{q\lambda} \hbar\omega_{q\lambda} \left( \langle n \rangle + \frac{1}{2} \right) = 3V \int \hbar\omega \left( \langle n \rangle + \frac{1}{2} \right) g(\omega) d\omega$$

Here

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Assume that the first Brillouin zone is a sphere with a radius  $q_D$ .

$$N = \sum_{q \in \text{BZ}} 1 = V \int_{q < q_D} \frac{d^3 q}{(2\pi)^3} = \frac{V}{(2\pi)^3} \frac{4\pi q_D^3}{3} = \frac{V q_D^3}{6\pi}$$

$$\Rightarrow V = \frac{6\pi^2 N}{q_D^3}$$

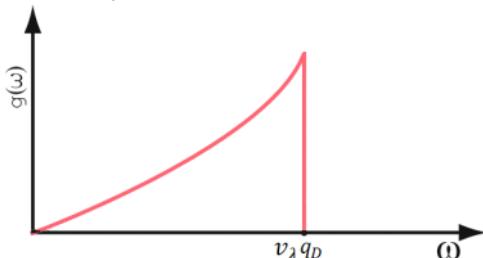
The density of states

$$\begin{aligned}
 g(\omega) &= \frac{1}{(2\pi)^3} \int \frac{dS}{|\nabla_q \omega_{q\lambda}|} \\
 &= \frac{1}{(2\pi)^3} \int \frac{q^2 \sin \theta d\theta d\phi}{v_\lambda} \\
 &= \frac{1}{(2\pi)^3} \frac{4\pi q^2}{v_\lambda} \\
 &= \frac{\omega^2}{2\pi^2 v_\lambda^3}
 \end{aligned}$$

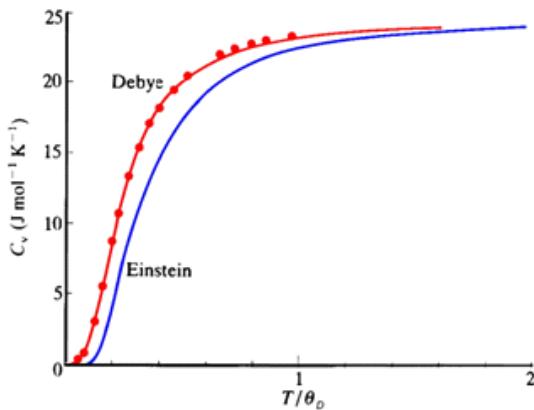
Since  $q \leq q_D$

$$g(\omega) = \frac{\omega^2}{2\pi^2 v_\lambda^3} \Theta(v_\lambda q_D - \omega) = \frac{3\omega^2}{2\pi^2 v^3} \Theta(\omega_D - \omega)$$

where  $v_\lambda q_D = \omega_D$



$$\begin{aligned}
 U &= 3 \frac{6\pi^2 N}{q_D^3} \int_0^\infty \left( \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} + \frac{\hbar\omega}{2} \right) \frac{\omega^2}{2\pi^2 v_s^3} \Theta(\omega_D - \omega) d\omega \\
 &= \frac{9N}{\omega_D^3} \int_0^{\omega_D} \left( \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1} + \frac{\hbar\omega^3}{2} \right) d\omega \\
 &= \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1} d\omega + \frac{9N\hbar\omega_D}{8} \\
 C_V &= \left( \frac{\partial U}{\partial T} \right)_V = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \frac{\hbar^2 \omega^4}{k_B T^2} d\omega
 \end{aligned}$$



### (3) Limit

1. Low-temperature limit:  $k_B T \ll \hbar\omega$

$$\text{Let } x = \frac{\hbar\omega}{k_B T} \Rightarrow dx = \frac{\hbar}{k_B T} d\omega$$

$$\begin{aligned} C_V &= 9Nk_B \left( \frac{k_B T}{\hbar\omega_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{e^{2x} - 2e^x + 1} dx \\ &= 9Nk_B \left( \frac{k_B T}{\hbar\omega_D} \right)^3 \int_0^{\infty} \frac{x^4}{e^x - 2 + e^{-x}} dx \\ &= 9Nk_B \left( \frac{k_B T}{\hbar\omega_D} \right)^3 \int_0^{\infty} \frac{x^4}{(e^x - 1)(1 - e^{-x})} dx \\ &= 9Nk_B \left( \frac{k_B T}{\hbar\omega_D} \right)^3 \frac{4\pi^4}{15} \\ &= \frac{12\pi^4}{5} Nk_B \left( \frac{k_B T}{\hbar\omega_D} \right)^3 \\ &\Rightarrow C_V \propto T^3 \end{aligned}$$

2. High-temperature limit:  $k_B T \gg \hbar\omega$

$$\begin{aligned} C_V &= 9Nk_B \left( \frac{k_B T}{\hbar\omega_D} \right)^3 \int_0^{x_D} \frac{x^4}{(e^x - 1)(1 - e^{-x})} dx \\ e^x - 1 &= (1 + x + \dots) - 1 \approx x \\ 1 - e^{-x} &= 1 - (1 - x + \dots) \approx x \\ \int_0^{x_D} \frac{x^4}{(e^x - 1)(1 - e^{-x})} dx &\approx \int_0^{x_D} \frac{x^4}{x^2} dx = \frac{x_D^3}{3} \end{aligned}$$

$$C_V = 9Nk_B \left(\frac{k_B T}{\hbar\omega_D}\right)^3 \frac{1}{3} \left(\frac{\hbar\omega_D}{k_B T}\right)^3 = 3Nk_B = 3R$$

# 5-1 Drude Theory

Tuesday, December 20, 2011 8:29 PM

## A. DRUDE ASSUMPTION (1900)

- (1) Define  $\tau$  the relaxation time between collisions.

In the presence of a constant electric field  $\vec{E}_0$

$$m \frac{d^2 \vec{r}}{dt^2} = -e \vec{E}_0 + \vec{F}_{\text{coll}}$$

Electrons make collisions every  $\tau$  second,

$$\vec{F}_{\text{coll}} = \frac{\Delta \vec{p}}{\Delta t} \approx -\frac{m \langle \vec{v} \rangle}{\tau}$$

Suppose that in each collision the electron's forward velocity is reduced to zero and then accelerated again after the collision, i.e.,  $\frac{d^2 \vec{r}}{dt^2} = 0$

Thus, we have

$$0 = -e \vec{E}_0 - \frac{m \langle \vec{v} \rangle}{\tau} \Rightarrow \langle \vec{v} \rangle \equiv \vec{v}_d = -\frac{e \vec{E}_0 \tau}{m}$$

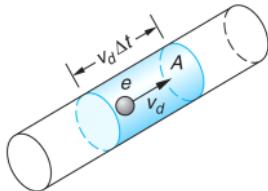
$$\tau = \frac{l}{v_d}, \text{ where } l \text{ is called the mean free path}$$

- (2) Electrons are treated as free particles moving with the velocity  $\vec{v}_d$  called drift velocity.

## B. CONDUCTIVITY

- (1) Ohm's law:

The current density:



$$\vec{j} = \frac{I}{A} = \frac{\Delta Q}{A \Delta t} = \frac{1}{A} \frac{(-ne)AL}{L/v_d} = -nev_d$$

where  $n$  is the electron density and  $L = v_d \Delta t$

$$\vec{j} = (-ne) \left( -\frac{e\vec{E}_0\tau}{m} \right) = \frac{ne^2\tau}{m} \vec{E}_0 = \sigma_0 \vec{E}_0$$

$$\Rightarrow \sigma_0 = \frac{ne^2\tau}{m} \dots \text{electrical conductivity}$$

OS:

From the electrical conductivity  $\tau \sim 10^{-14} - 10^{-15} \text{ s}$ .

The average velocity at room temperature  $\frac{1}{2}mv^2 = \frac{3}{2}k_B T \Rightarrow v \sim 10^5 \text{ m/s}$ .

The mean free path  $l = v\tau \sim 1 - 10 \text{ \AA} \sim \text{interatomic spacing}$ .

## (2) AC conductivity

$$m \frac{d\vec{v}_d(t)}{dt} = -e\vec{E} - m \frac{\vec{v}_d(t)}{\tau}$$

Let  $\vec{E}(t) = \vec{E}_0 e^{-i\omega t}$  and  $\vec{v}_d(t) = \vec{v}_d e^{-i\omega t}$

$$-mi\omega\vec{v}_d e^{-i\omega t} = -e\vec{E}_0 e^{-i\omega t} - m \frac{\vec{v}_d}{\tau} e^{-i\omega t}$$

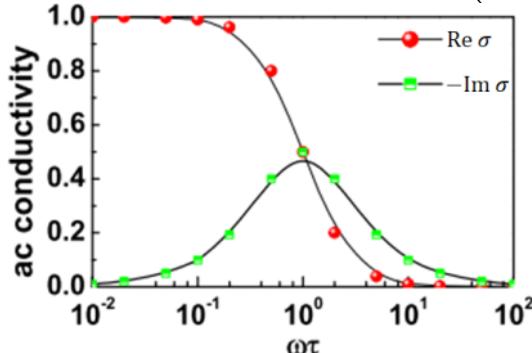
$$\Rightarrow mi\omega\vec{v}_d = e\vec{E}_0 + m \frac{\vec{v}_d}{\tau}$$

$$\Rightarrow i\omega\tau\vec{v}_d = \frac{e\tau}{m}\vec{E}_0 + \vec{v}_d$$

$$\Rightarrow \vec{v}_d = \frac{-1}{1 - i\omega\tau} \frac{e\tau}{m} \vec{E}_0$$

$$\vec{j} = -ne\vec{v}_d = \frac{1}{1 - i\omega\tau} \frac{ne^2\tau}{m} \vec{E}_0 = \sigma(\omega) \vec{E}_0$$

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} = \sigma_0 \frac{1 + i\omega\tau}{1 + \omega^2\tau^2} = \sigma_0 \left( \frac{1}{1 + \omega^2\tau^2} + i \frac{\omega\tau}{1 + \omega^2\tau^2} \right)$$



## (3) Plasma frequency

In a region with no charge, Maxwell's equations are

$$\left\{ \begin{array}{l} \nabla \cdot \vec{E} = 0 \\ \nabla \cdot \vec{B} = 0 \\ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \\ \nabla \times \vec{B} = \mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t} \\ \text{L.H.S.: } \nabla \times (\nabla \times \vec{E}) = -\nabla^2 \vec{E} \\ \text{R.H.S.: } \nabla \times (\nabla \times \vec{E}) = -\frac{\partial}{\partial t} (\nabla \times \vec{B}) = -\frac{\partial}{\partial t} \left( \mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t} \right) \end{array} \right.$$

Assume  $\vec{E}(x, t) = \vec{E}(x)e^{-i\omega t}$

$$\vec{J} = \sigma(\omega) \vec{E}(x) e^{-i\omega t}$$

$$-\nabla^2 \vec{E}(x) e^{-i\omega t} = i\omega \mu_0 \sigma(\omega) \vec{E}(x) e^{-i\omega t} + \frac{\omega^2}{\mu_0 \epsilon_0} \vec{E}(x) e^{-i\omega t}$$

where  $\mu_0 \epsilon_0 = 1/c^2$

$$\Rightarrow \nabla^2 \vec{E}(x) = -i\omega \mu_0 \sigma(\omega) \vec{E}(x) - \frac{\omega^2}{\mu_0 \epsilon_0} \vec{E}(x)$$

$$\Rightarrow \nabla^2 \vec{E}(x) + \frac{\omega^2}{\mu_0 \epsilon_0} \left( 1 + \frac{i\sigma(\omega)}{\omega \epsilon_0} \right) \vec{E}(x) = 0$$

Since  $\mu_0 \epsilon_0 = 1/c^2$

$$\nabla^2 \vec{E}(x) + \frac{\omega^2}{c^2} \left( 1 + \frac{i\sigma(\omega)}{\omega \epsilon_0} \right) \vec{E}(x) = 0$$

The complex dielectric constant

$$\begin{aligned} \epsilon(\omega) &= 1 + \frac{i}{\omega \epsilon_0} \sigma(\omega) \\ &= 1 + \frac{i\sigma_0}{\omega \epsilon_0} \left( \frac{1}{1 + \omega^2 \tau^2} + i \frac{\omega \tau}{1 + \omega^2 \tau^2} \right) \\ &= 1 - \frac{\sigma_0}{\epsilon_0} \frac{\tau}{1 + \omega^2 \tau^2} + i \frac{\sigma_0}{\epsilon_0} \frac{1/\omega}{1 + \omega^2 \tau^2} \end{aligned}$$

In the limit  $\omega \tau \gg 1$

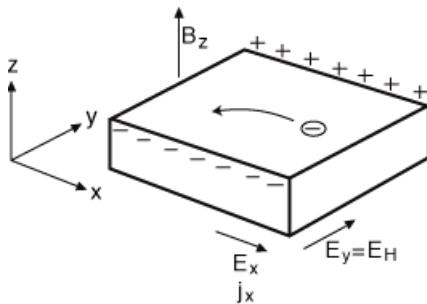
$$\text{Re } \epsilon(\omega) = 1 - \frac{ne^2 \tau}{m \epsilon_0} \frac{\tau}{1 + \omega^2 \tau^2} \approx 1 - \frac{ne^2}{m \epsilon_0 \omega^2}$$

Let  $\omega_p^2 = \frac{ne^2}{m \epsilon_0}$  be the plasma frequency

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

## C. HALL EFFECT (1879)

- (1) In the presence of a magnetic field (weak  $B$  field) and an electric field  $\vec{E}$



The Lorentz force:

$$\vec{F} = -e \left( \vec{E} + \frac{1}{c} \vec{v}_d \times \vec{B} \right)$$

Under the magnetic field, the electron moves circularly. The centrifugal force is equal to the Lorentz force and the cyclotron frequency  $\omega_c$  is

$$\frac{ev_d B}{c} = m \frac{v_d^2}{r} \Rightarrow v_d = \frac{reB}{mc}$$

$$\Rightarrow \omega_c = 2\pi \cdot \frac{v_d}{2\pi r} = \frac{eB}{mc} \dots \text{cyclotron frequency}$$

The Newton's equations are

$$\begin{aligned} \frac{m\vec{v}_d}{\tau} &= -e\vec{E} - \frac{e}{c} \vec{v}_d \times \vec{B} \\ &= -e\vec{E} - \frac{eB}{c} \vec{v}_d \times \hat{z} \\ &= -e\vec{E} - m \frac{eB}{mc} \vec{v}_d \times \hat{z} \\ &= -e\vec{E} - m\omega_c \vec{v}_d \times \hat{z} \end{aligned}$$

$$\begin{cases} m \frac{v_x}{\tau} = -eE_x - m\omega_c v_y \\ m \frac{v_y}{\tau} = -eE_y + m\omega_c v_x \end{cases}$$

$$\begin{cases} v_x = -\frac{e\tau/m}{1 + (\omega_c\tau)^2} (E_x - \omega_c\tau E_y) \\ v_y = -\frac{e\tau/m}{1 + (\omega_c\tau)^2} (\omega_c\tau E_x + E_y) \end{cases}$$

The external magnetic field induce an effective electric field  $E_y$ . The induced field  $E_y$  is coupled to  $E_x$ .

(2) The conductivity tensor  $\bar{\sigma}$  and resistivity tensor  $\bar{\rho}$

$$\begin{cases} j_x = -env_x = \frac{\sigma_0}{1 + (\omega_c \tau)^2} (E_x - \omega_c \tau E_y) \\ j_y = -env_y = \frac{\sigma_0}{1 + (\omega_c \tau)^2} (\omega_c \tau E_x + E_y) \end{cases}$$

$$\begin{cases} j_x = \sigma_{xx} E_x + \sigma_{xy} E_y \\ j_y = \sigma_{yx} E_x + \sigma_{yy} E_y \end{cases}$$

$$\vec{j} = \bar{\sigma} \cdot \vec{E} \Rightarrow \begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

$$\sigma_{xx} = \sigma_{yy} = \frac{\sigma_0}{1 + (\omega_c \tau)^2}$$

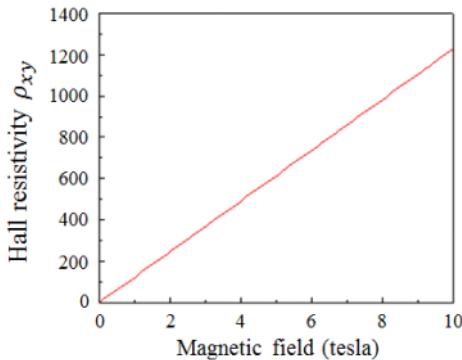
$$\sigma_{xy} = -\sigma_{yx} = -\frac{\omega_c \tau \sigma_0}{1 + (\omega_c \tau)^2}$$

$$\bar{\rho} = \bar{\sigma}^{-1} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix}^{-1} = \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ \rho_{yx} & \rho_{yy} \end{pmatrix}$$

$$\rho_{xx} = \rho_{yy} = \frac{\sigma_{yy}}{\sigma_{xx} \sigma_{yy} - \sigma_{xy} \sigma_{yx}} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2} = \frac{1}{\sigma_0}$$

(3) Hall resistivity

$$\rho_{xy} = -\rho_{yx} = -\frac{\sigma_{xy}}{\sigma_{xx} \sigma_{yy} - \sigma_{xy} \sigma_{yx}} = -\frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2} = \frac{\omega_c \tau}{\sigma_0} = \frac{B}{nec}$$



## D. THERMAL PROPERTIES

(1) Specific heat:

$$C_v = \frac{1}{V} \frac{d\langle E \rangle}{dT}$$

Electrons are considered as gas following Boltzmann statistics.

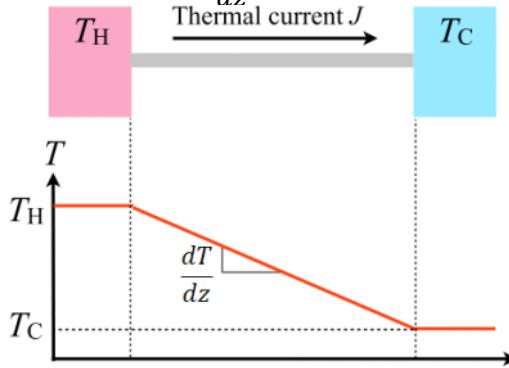
$$\langle E \rangle = \mathcal{V} \int_0^{\infty} \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon = \mathcal{V} \int_0^{\infty} \frac{3}{2} k_B T \times \frac{N e^{-\beta \varepsilon}}{Z} \times \frac{1}{\mathcal{V}} d\varepsilon = \frac{3}{2} N k_B T$$

$$C_v = \frac{1}{\mathcal{V}} \frac{d\langle E \rangle}{dT} = \frac{3}{2} n k_B$$

- (2) Thermal conductivity:

Fourier's Law (1822): The ratio of the thermal current to the magnitude of the temperature gradient,

$$\vec{j} = -\kappa \nabla T = -\kappa \frac{dT}{dz}$$

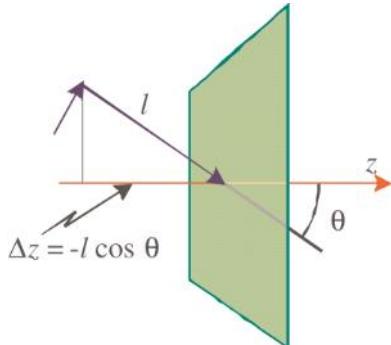


From the kinetic theory, the thermal current (energy flux) is

$$\vec{j} = \int \varepsilon \vec{v} f(v) d^3 v = \int C_v \Delta T \vec{v} f(v) d^3 v = \int \left( C_v \frac{dT}{dz} \Delta z \right) \vec{v} f(v) d^3 v$$

where  $f(v)$  is the Maxwell-Boltzmann velocity distribution.

The energy flux along the  $z$ -direction



Let  $\Delta z = -l \cos \theta = -v\tau \cos \theta$

$$\begin{aligned}
j_z &= \int \left( C_v \frac{dT}{dz} \Delta z \right) \vec{v} f(v) d^3 v \\
&= \int \left( -C_v \frac{dT}{dz} v \tau \cos \theta \right) v \cos \theta f(v) d^3 v \\
&= -\tau C_v \frac{dT}{dz} \int v^2 \cos^2 \theta f(v) d^3 v
\end{aligned}$$

Since  $d^3 v = v^2 dv \sin \theta d\theta d\phi$

$$j_z = -2\pi\tau C_v \frac{dT}{dz} \int v^2 f(v) v^2 dv \int_0^\pi \cos^2 \theta \sin \theta d\theta$$

Since  $\int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{2}{3}$

$$j_z = -2\pi\tau C_v \frac{dT}{dz} \int v^2 f(v) v^2 dv \times \frac{2}{3} = -\frac{4\pi}{3} \tau C_v \frac{dT}{dz} \int v^2 f(v) v^2 dv$$

Let  $\bar{v^2} = \int v^2 f(v) 4\pi v^2 dv$

$$j_z = -\frac{1}{3} \tau C_v \frac{dT}{dz} \bar{v^2} = -\kappa \frac{dT}{dz}$$

The thermal conductivity:

$$\kappa = \frac{1}{3} \tau C_v \bar{v^2} = \frac{2}{3m} \tau \left( \frac{3}{2} n k_B \right) \left( \frac{1}{2} m \bar{v^2} \right) = \frac{3}{2} \frac{n \tau k_B^2 T}{m}$$

### (3) Wiedermann-Franz law (1853):

At a given temperature the ratio of the thermal conductivity to the electric conductivity was the same for all metals.

Lorentz number  $L = \frac{\kappa}{\sigma_0 T} = \text{constant}$

$$L = \frac{\kappa}{\sigma_0 T} = \frac{\frac{3}{2} \frac{n \tau k_B^2 T}{m}}{\frac{ne^2 \tau}{m}} \frac{1}{T} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2 = 1.11 \times 10^{-8} \text{ W}\Omega/\text{K}^2$$

OS:

$$\text{Lorentz number } L = \frac{\kappa}{\sigma T} = 2.43 \times 10^{-8} \text{ W}\Omega/\text{K}^2$$

This empirical law is named after Gustav Wiedemann and Rudolph Franz, who in 1853 reported that  $\kappa/\sigma$  has approximately the same value for different metals at the same temperature. The proportionality of  $\kappa/\sigma$  with temperature was discovered by Ludvig Lorenz in 1872.

## E. OUTCOME OF DRUDE MODEL

### (1) Successes

Dc conductivity

$$\sigma_0 = \frac{ne^2\tau}{m}$$

Ac conductivity

$$\sigma(\omega) = \sigma_0 \left( \frac{1}{1 + \omega^2\tau^2} + i \frac{\omega\tau}{1 + \omega^2\tau^2} \right)$$

Plasma frequency

$$\omega_p^2 = \frac{ne^2}{m\epsilon_0}$$

Hall effect

$$\rho_{xy} = \frac{B}{nec}$$

Electronic thermal conductivity

$$\kappa = \frac{3}{2} \frac{n\tau k_B T}{m}$$

Wiedermann-Franz law

### (2) Shortcoming

Specific heat

$$C_v = \frac{3}{2} nk_B$$

OS:

The success of the Drude's model in predicting the Wiedemann-Franz law is a consequence of the cancellation of two errors: at room temperature, the actual electronic specific heat is 100 times smaller than the Drude's prediction, but the velocity of the particles taken into account is 10 times larger.

# 5-2 Sommerfeld Theory

Tuesday, December 20, 2011 8:30 PM

## A. QUANTUM THEORY OF ELECTRON GAS (1928)

OS:

Arnold Johannes Wilhelm Sommerfeld (1868-1951)

- (1) As the freely moving electrons cannot escape the surface of the material, they may be treated as particles confined (trapped) in a box of volume  $\mathcal{V} = L_x L_y L_z$ .

The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_{n,k}(\vec{r}) = \varepsilon_{n,k} \psi_{n,k}(\vec{r})$$

- (2) The eigenfunctions  $\psi_{n,k}$  and eigenenergies  $\varepsilon_{n,k}$

- With periodic boundary conditions (Born-von Karman boundary conditions)

$$\psi_{n,k}(\vec{r}) = A_n e^{i\vec{k} \cdot \vec{r}} \text{ and } \varepsilon_{n,k} = \frac{\hbar^2 k^2 n^2}{2m}$$

$$\text{Since } \psi_{n,k}(\vec{r} + \vec{L}) = \psi_{n,k}(\vec{r})$$

$$\Rightarrow A e^{i\vec{k} \cdot (\vec{r} + \vec{L})} = A e^{i\vec{k} \cdot \vec{r}} \Rightarrow e^{i\vec{k} \cdot \vec{L}} = 1$$

$$\Rightarrow k_x = \frac{2\pi n_x}{L_x}, \quad k_y = \frac{2\pi n_y}{L_y}, \quad k_z = \frac{2\pi n_z}{L_z}$$

$$\Rightarrow \Delta k_i = \frac{2\pi}{L_i}$$



Box normalization conditions:

$$\int_0^{\mathcal{V}} \psi_{n,k}^*(\vec{r}) \psi_{n,k}(\vec{r}) d^3r = A_n^2 \mathcal{V} = 1 \Rightarrow A_n = \frac{1}{\sqrt{\mathcal{V}}}$$

$$\Rightarrow \psi_{n,k}(\vec{r}) = \frac{1}{\sqrt{\mathcal{V}}} e^{i\vec{k} \cdot \vec{r}}$$

- With open boundary conditions

$$\psi_{n,k}(\vec{r}) = A_n \sin \vec{k} \cdot \vec{r} + B_n \cos \vec{k} \cdot \vec{r} \text{ and } \varepsilon_{n,k} = \frac{\hbar^2 k^2 n^2}{2m}$$

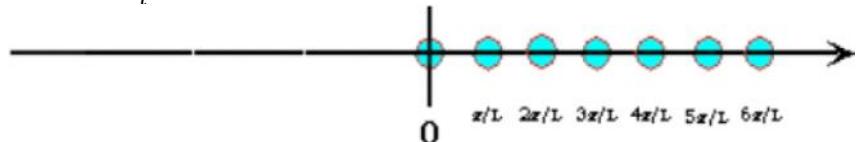
Since  $\psi_{n,k}(\vec{r})$  vanishes at the boundary

$$\psi_{n,k}(0) = 0 \Rightarrow B_n = 0 \Rightarrow \psi_{n,k}(\vec{r}) = A_n \sin \vec{k} \cdot \vec{r}$$

$$\psi_{n,k}(L) = 0 \Rightarrow A_n \sin \vec{k} \cdot \vec{L} = 0 \Rightarrow \vec{k} \cdot \vec{L} = \pi\ell$$

$$\Rightarrow k_x = \frac{\pi\ell_x}{L_x}, \quad k_y = \frac{\pi\ell_y}{L_y}, \quad k_z = \frac{\pi\ell_z}{L_z}$$

$$\Rightarrow \Delta k_i = \frac{\pi}{L_i}$$



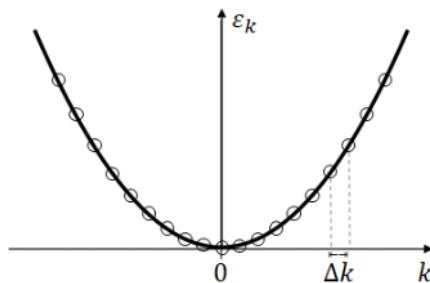
Normalization conditions:

$$\int_0^V \psi_{n,k}^*(\vec{r}) \psi_{n,k}(\vec{r}) d^3r = A_n^2 \frac{2}{L_x} \frac{2}{L_y} \frac{2}{L_z} = 1 \Rightarrow A_n = \sqrt{\frac{8}{V}}$$

$$\Rightarrow \psi_{n,k}(\vec{r}) = \sqrt{\frac{8}{V}} \sin k_x x \sin k_y y \sin k_z z$$

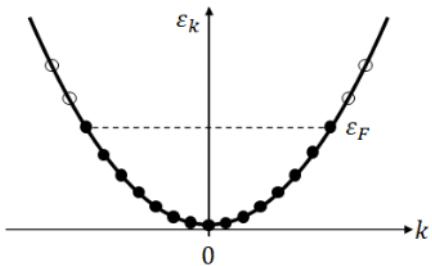
## B. GROUND STATE CONFIGURATION

- (1) Energy band for  $n = 1 \Rightarrow \varepsilon_{1,k} \equiv \varepsilon_k = \hbar^2 k^2 / 2m$



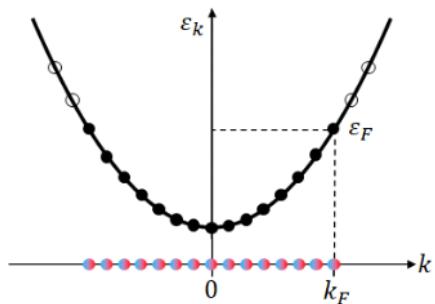
Place electrons from the energy level  $\vec{k} = 0$ . Then continue to add electrons, subject to the Pauli exclusion principle, and successively filling the energy levels of lowest energy that are empty.

- (2) Fermi energy



The energy levels of  $\varepsilon_k \leq \varepsilon_F$  are occupied subject to the Pauli exclusion principle, and all those with  $\varepsilon_k > \varepsilon_F$  are empty.  $\varepsilon_F$  is called Fermi energy.

### (3) Fermi surface



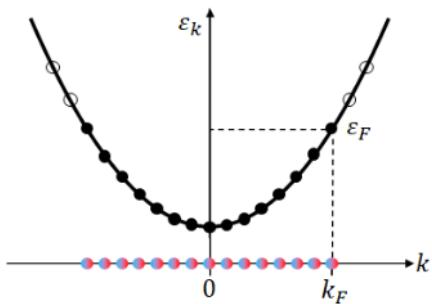
In the first Brillouin zone, the states  $|\vec{k}| \leq |\vec{k}_F|$  are occupied subject to the Pauli exclusion principle, and all those with  $|\vec{k}| > |\vec{k}_F|$  are empty.  $\vec{k}_F$  is called Fermi wave vector. The locus of points in the first Brillouin zone where  $\varepsilon_k = \varepsilon_F$  is called Fermi surface.

### EXAMPLES:

Consider a simple metal

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

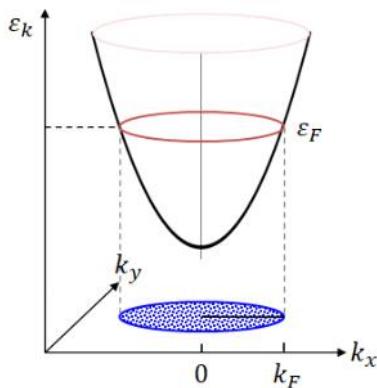
(a) For 1D case:



The Fermi surface is two points at  $|\vec{k}| = |\vec{k}_F|$ .

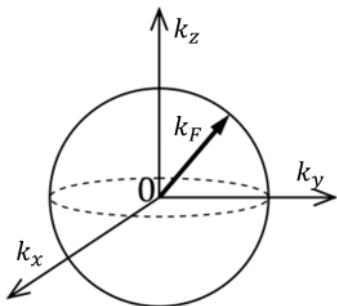
- (b) For 2D case:

The Fermi surface is a circle.



- (c) For 3D case:

The Fermi surface is a sphere.

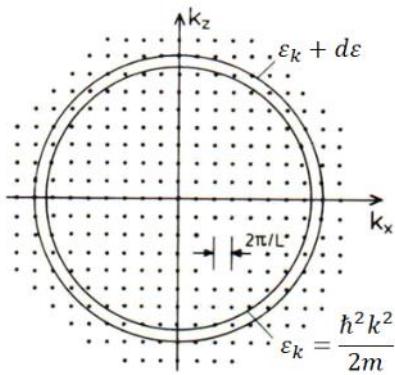


- (4) The total number of electrons  $N$  at zero temperature

= The total number of unit cells [c.f.2-2-B]

= The total number of occupied states at zero temperature

1. Periodic boundary conditions:

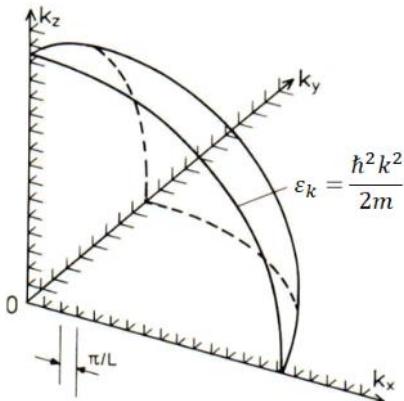


$$N = 2 \times \frac{\frac{4\pi}{3} k_F^3}{\left(\frac{2\pi}{L}\right)^3} \Rightarrow \frac{N}{V} = \frac{k_F^3}{3\pi^2} = n$$

OS:

$$N = 2 \sum_{|k| \leq k_F} 1 = 2V \int_0^{k_F} \frac{d^3 k}{(2\pi)^3} = \frac{2V}{(2\pi)^3} 4\pi \frac{k_F^3}{3} = V \frac{k_F^3}{3\pi^2}$$

2. Open boundary conditions:



$$N = 2 \times \frac{1}{8} \times \frac{\frac{4\pi}{3} k_F^3}{\left(\frac{\pi}{L}\right)^3} \Rightarrow \frac{N}{V} = \frac{k_F^3}{3\pi^2} = n$$

$$\Rightarrow k_F = (3\pi^2 n)^{1/3}$$

(5) The ground state energy

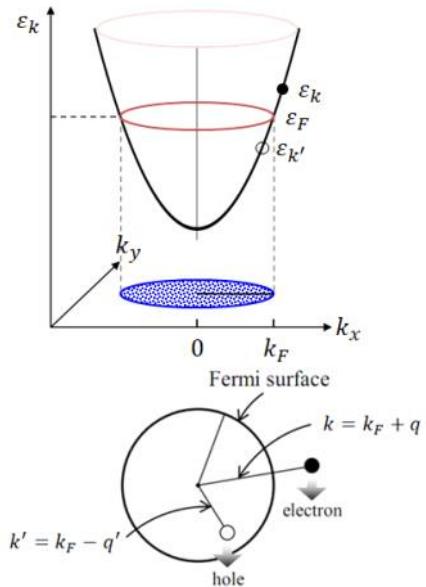
$$E = 2 \sum_{k \leq k_F} \epsilon_k = 2V \int_0^{k_F} \frac{\hbar^2 k^2}{2m} \frac{d^3 k}{(2\pi)^3} = \frac{V \hbar^2}{(2\pi)^3 m} \int k^2 k^2 dk d\Omega = \frac{V \hbar^2 k_F^5}{10\pi^2 m}$$

Average energy per electron is

$$\frac{E}{N} = \frac{\mathcal{V} \frac{\hbar^2 k_F^5}{10\pi^2 m}}{\mathcal{V} \frac{k_F^3}{3\pi^2}} = \frac{3 \hbar^2 k_F^2}{5 \cdot 2m} = \frac{3}{5} \varepsilon_F$$

## C. HOLES

- (1) When an electron is excited to states above the Fermi energy, we define that the absence of an electron with energy  $\varepsilon_k$ , momentum  $\hbar k$  and charge  $e$  corresponds to the presence of a hole with energy  $\varepsilon_{k'} = -\varepsilon_k$ , momentum  $-\hbar k$  and charge  $-e$ .



## 5-3 Density of States of Electrons

Tuesday, December 20, 2011 8:30 PM

- **Electron density in real space:**

The electron density allows us to know the molecular structure from which a crystal is made. Thus the electron density provides important understanding of materials.

- **Density of states in reciprocal space:**

The number of active electrons  $dn$  is related to the characteristics of a crystal. Since  $dn = g(\varepsilon)d\varepsilon$ , thus, knowing the density of states  $g(\varepsilon)$  is able to understand properties of a crystal.

### A. ONE-DIMENSIONAL METAL

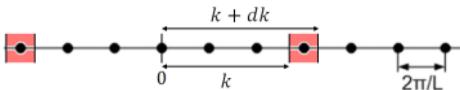
(1) Direct integral:

$$g(\varepsilon) = 2 \sum_k \delta(\varepsilon - \varepsilon_k) = \frac{2}{2\pi} \int \delta(\varepsilon - \varepsilon_k) dk = \frac{1}{\pi} \int_{-\infty}^{\infty} \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) dk$$

Since  $\delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) = \frac{\delta(k - \sqrt{2m\varepsilon/\hbar^2})}{|\hbar^2 k/m|} + \frac{\delta(k + \sqrt{2m\varepsilon/\hbar^2})}{|\hbar^2 k/m|}$

$$\begin{aligned} g(\varepsilon) &= \frac{1}{\pi} \int_{-\infty}^{\infty} \left[ \frac{\delta(k - \sqrt{2m\varepsilon/\hbar^2})}{|\hbar^2 k/m|} + \frac{\delta(k + \sqrt{2m\varepsilon/\hbar^2})}{|\hbar^2 k/m|} \right] dk \\ &= \frac{1}{\pi \hbar^2 \sqrt{2m\varepsilon/\hbar^2}} \cdot \frac{2m}{\sqrt{2m\varepsilon/\hbar^2}} \\ &= \frac{\sqrt{2m}}{\pi \hbar} \frac{1}{\sqrt{\varepsilon}} \end{aligned}$$

(2) Counting  $k$  values:



Number of filled states in a Fermi line segment:

$$N(k) = 2 \times \frac{2k}{2\pi/L} = \frac{2Lk}{\pi}$$

where  $2\pi/L$  is the length of a state occupied and  $2k$  is the length of a Fermi interval (here, in 1D, it is a line segment).

$$\text{Since } \varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \frac{\sqrt{2m\varepsilon}}{\hbar}$$

$$N(\varepsilon) = \frac{2L\sqrt{2m\varepsilon}}{\pi\hbar} = \frac{2L\sqrt{2m}}{\pi\hbar}\sqrt{\varepsilon}$$

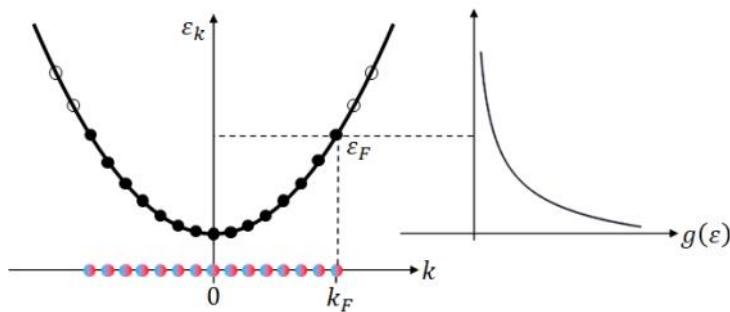
$$g(\varepsilon) = \frac{1}{L} \frac{dN(\varepsilon)}{d\varepsilon} = \frac{2\sqrt{2m}}{\pi\hbar} \frac{d\sqrt{\varepsilon}}{d\varepsilon} = \frac{\sqrt{2m}}{\pi\hbar} \frac{1}{\sqrt{\varepsilon}}$$

Alternative method:

Using the Jacobian  $g(\varepsilon)d\varepsilon = g(k)dk$

$$g(k) = \frac{1}{L} \frac{dN(k)}{dk} = \frac{2}{\pi} \frac{dk}{dk} = \frac{2}{\pi}$$

$$g(\varepsilon) = g(k) \frac{dk}{d\varepsilon} = \frac{2}{\pi} \frac{dk}{d\varepsilon} = \frac{2}{\pi} \frac{\sqrt{2m}}{\hbar} \frac{d\sqrt{\varepsilon}}{d\varepsilon} = \frac{\sqrt{2m}}{\pi\hbar} \frac{1}{\sqrt{\varepsilon}}$$



(3) Surface integral:

$$\nabla_k \varepsilon_k = \frac{\hbar^2 k}{m}$$

$$g(\varepsilon) = \frac{2}{2\pi} \int \frac{dS_E}{|\nabla_k \varepsilon_k|} = \frac{2}{2\pi} \frac{2}{\hbar^2 k/m} = \frac{\sqrt{2m}}{\pi\hbar} \frac{1}{\sqrt{\varepsilon}}$$

## B. TWO-DIMENSIONAL METAL

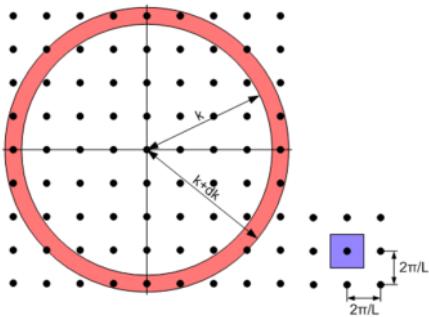
(1) Direct integral:

$$\begin{aligned}
g(\varepsilon) &= \frac{2}{(2\pi)^2} \int \delta(\varepsilon - \varepsilon_k) d^2k \\
&= \frac{1}{2\pi^2} \int_0^\infty \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) 2\pi k dk \\
&= \frac{1}{\pi} \int_0^\infty \frac{\delta\left(k - \sqrt{2m\varepsilon/\hbar^2}\right)}{|\hbar^2 k/m|} k dk \\
&= \frac{1}{\pi} \frac{1}{\hbar^2/m} \\
&= \frac{m}{\pi\hbar^2}
\end{aligned}$$

Alternative method:

$$\begin{aligned}
g(\varepsilon) &= \frac{1}{2\pi^2} \int_0^\infty \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) 2\pi k dk \\
&= \frac{1}{2\pi} \int_0^\infty \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) dk^2 \\
&= \frac{1}{2\pi} \frac{2m}{\hbar^2} \\
&= \frac{m}{\pi\hbar^2}
\end{aligned}$$

(2) Counting  $k$  values:



Number of filled states in a Fermi circle:

$$N(k) = 2 \times \frac{\pi k^2}{(2\pi/L)^2} = \frac{L^2 k^2}{2\pi}$$

where  $(2\pi/L)^2$  is the area of a state occupied and  $\pi k^2$  is the area of a Fermi circle.

$$\text{Since } \varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \frac{\sqrt{2m\varepsilon}}{\hbar}$$

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

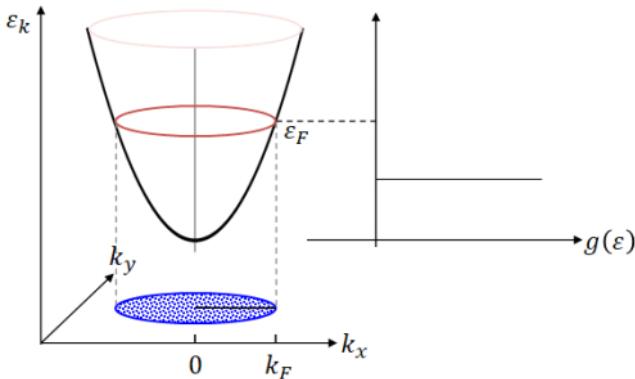
$$\Rightarrow g(\varepsilon) = \frac{1}{L^2} \frac{dN(\varepsilon)}{d\varepsilon} = \frac{m}{\pi \hbar^2} \frac{d\varepsilon}{d\varepsilon} = \frac{m}{\pi \hbar^2}$$

Alternative method:

Using the Jacobian  $g(\varepsilon)d\varepsilon = g(k)dk$

$$g(k) = \frac{1}{L^2} \frac{dN(k)}{dk} = \frac{1}{2\pi} \frac{dk^2}{dk} = \frac{k}{\pi}$$

$$g(\varepsilon) = g(k) \frac{dk}{d\varepsilon} = \frac{k}{\pi} \frac{dk}{d\varepsilon} = \frac{1}{\pi} \frac{\sqrt{2m\varepsilon}}{\hbar} \frac{\sqrt{2m}}{\hbar} \frac{d\sqrt{\varepsilon}}{d\varepsilon} = \frac{2m\sqrt{\varepsilon}}{\pi \hbar^2} \frac{1}{2\sqrt{\varepsilon}} = \frac{m}{\pi \hbar^2}$$



(3) Surface integral:

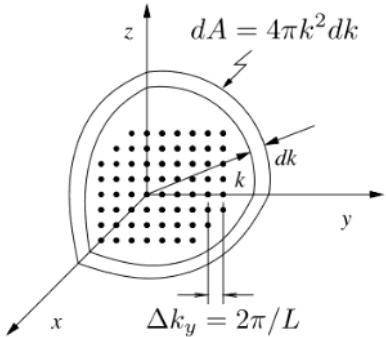
$$g(\varepsilon) = \frac{2}{(2\pi)^2} \int \frac{dS_E}{|\nabla_k \varepsilon_k|} = \frac{2}{4\pi^2} \frac{2\pi k}{\hbar^2 k/m} = \frac{m}{\pi \hbar^2}$$

## C. THREE-DIMENSIONAL METAL

(1) Direct integral:

$$\begin{aligned}
g(\varepsilon) &= \frac{2}{(2\pi)^3} \int \delta(\varepsilon - \varepsilon_k) d^3k \\
&= \frac{1}{4\pi^3} \int_0^\infty \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) 4\pi k^2 dk \\
&= \frac{1}{\pi^2} \int_0^\infty \frac{\delta\left(k - \sqrt{2m\varepsilon/\hbar^2}\right)}{|\hbar^2 k/m|} k^2 dk \\
&= \frac{1}{\pi^2} \frac{\sqrt{2m\varepsilon/\hbar^2}}{\hbar^2/m} \\
&= \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}
\end{aligned}$$

(2) Counting  $k$  values:



Number of filled states in a Fermi sphere:

$$N(k) = 2 \times \frac{\frac{4}{3}\pi k^3}{(2\pi/L)^3} = \frac{\mathcal{V} k^3}{3\pi^2}$$

where  $(2\pi/L)^3$  is the volume of a state occupied and  $4\pi k^3/3$  is the volume of a Fermi sphere.

$$\text{Since } \varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \frac{\sqrt{2m\varepsilon}}{\hbar}$$

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

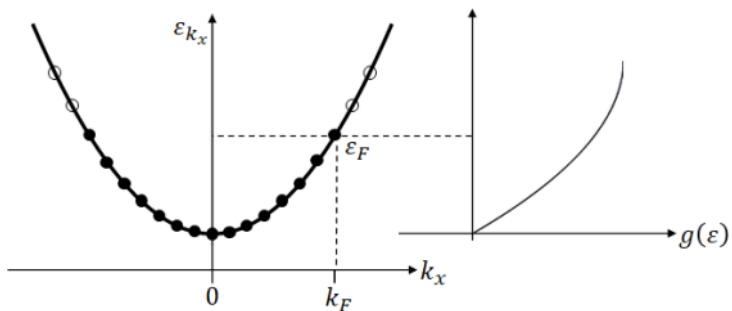
$$g(\varepsilon) = \frac{1}{\mathcal{V}} \frac{dN(\varepsilon)}{d\varepsilon} = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{d\varepsilon^{3/2}}{d\varepsilon} = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}$$

**Alternative method:**

Using the Jacobian  $g(\varepsilon)d\varepsilon = g(k)dk$

$$g(k) = \frac{1}{\mathcal{V}} \frac{dN(k)}{dk} = \frac{1}{3\pi^2} \frac{dk^3}{dk} = \frac{k^2}{\pi^2}$$

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



(3) Surface integral:

$$g(\varepsilon) = \frac{2}{(2\pi)^3} \int \frac{dS_E}{|\nabla_k \varepsilon_k|} = \frac{2}{8\pi^3} \frac{4\pi k^2}{\hbar^2 k/m} = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon}$$

# 5-4 Thermal Properties of Electrons

Tuesday, December 20, 2011 8:30 PM

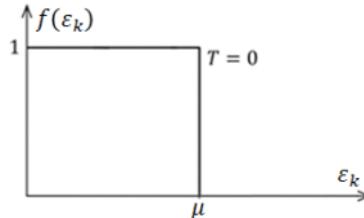
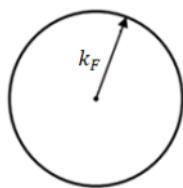
## A. DISTRIBUTION FUNCTION OF ELECTRONS

- (1) The probability that a given energy state is occupied by electrons follows the Fermi distribution:

$$f(\varepsilon_k) = \frac{1}{e^{(\varepsilon_k - \mu)/k_B T} + 1}$$

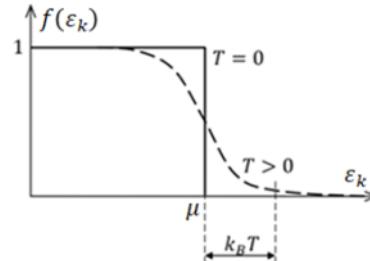
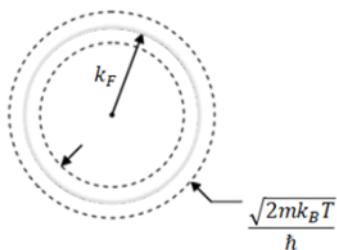
where  $\mu$  is the chemical potential (the increased free energy needed to add an electron to the system).

At zero temperature, all electrons occupy states within the Fermi surface or below the Fermi energy  $\mu = \varepsilon_F$ , which corresponds to a Fermi function with a sharp occupancy cut-off at Fermi energy.



$$f(\varepsilon_k) = \frac{1}{e^{(\varepsilon_k - \mu)/k_B T} + 1} = \begin{cases} 1, & \varepsilon < \mu \\ \frac{1}{2}, & \varepsilon = \mu \\ 0, & \varepsilon > \mu \end{cases}$$

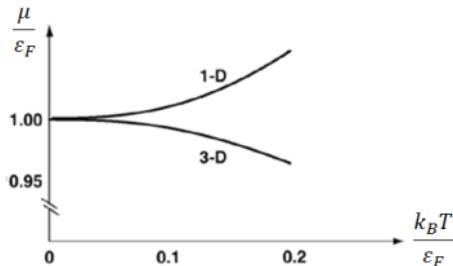
At finite temperature, some of the electrons will be excited from the states beneath the Fermi surface to the states above the Fermi surface, i.e., some electrons will be excited to states above Fermi energy.



The Fermi distribution smooths out around the Fermi energy.

EXAMPLES:

1. The chemical potential as a function of  $T$



Typical values of a metal at low temperature

$$n = 10^{23} \text{ cm}^{-3}$$

$$\text{Fermi energy: } \varepsilon_F = \hbar^2 k_F^2 / 2m \approx 5 \text{ eV}$$

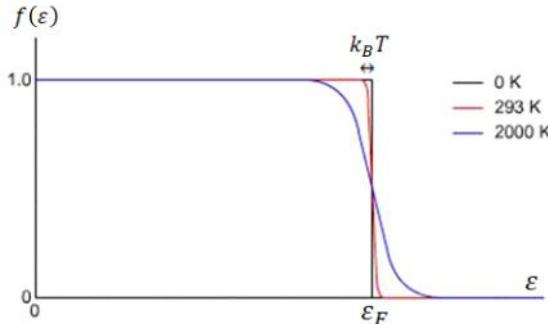
$$\text{Fermi temperature: } T_F = \varepsilon_F / k_B \approx 10^5 \text{ K}$$

$$\text{Fermi velocity: } v_F \approx 10^8 \text{ cm/sec}$$

$\Rightarrow \mu$  can be considered as constant at  $T \leq 1000 \text{ K}$

(2) Active electrons at temperature  $T$ :

Only a relatively small number of electrons  $\Delta N$  in the energy range of order  $k_B T$ , centered on  $\varepsilon_F$  do contribute to the macroscopic properties.



The fraction of active electrons is about

$$\frac{\Delta N(\varepsilon_F)}{N}$$

where

$N$  = the total number of electrons at finite temperature

= the total number of occupied states at finite temperature

$$= \sum_k n_k$$

$$= \frac{\mathcal{V}}{(2\pi)^3} \int n_k d^3k$$

$$= \mathcal{V} \int f(\varepsilon) g(\varepsilon) d\varepsilon$$

$$= \frac{\mathcal{V}}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{\varepsilon}}{e^{(\varepsilon-\mu)/k_B T} + 1} d\varepsilon$$

OS:

Cannot be integrated out, except the numerical method.

Since the total number of electrons  $N$  is same at zero temperature and finite temperature, i.e.,  $f(\varepsilon) = 1$  for  $\varepsilon < \mu = \varepsilon_F$

$$N = \frac{\mathcal{V}}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon = \frac{\mathcal{V}}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{3} \varepsilon_F^{3/2}$$

$$\Delta N(\varepsilon_F) = \mathcal{V} \int_{\varepsilon - \varepsilon_F}^{\varepsilon + \varepsilon_F} f(\varepsilon) g(\varepsilon) d\varepsilon \approx \mathcal{V} f(\varepsilon_F) g(\varepsilon_F) 2k_B T$$

Since

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

$$\Delta N(\varepsilon_F) = \mathcal{V} \times \frac{1}{2} \times \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} \times 2k_B T = \frac{\mathcal{V}}{2\pi^2} (k_B T) \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F}$$

The fraction of active electrons is about

$$\frac{\Delta N(\varepsilon_F)}{N} = \frac{\frac{\mathcal{V}}{2\pi^2} (k_B T) \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F}}{\frac{\mathcal{V}}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{3} \varepsilon_F^{3/2}} = \frac{3 k_B T}{2 \varepsilon_F} = \frac{3 k_B T}{2 k_B T_F} = \frac{3 T}{2 T_F}$$

At room temperature, for a typical metal, the fraction is

$$\frac{\Delta N(\varepsilon_F)}{N} = \frac{3T}{2T_F} \approx 0.015$$

We are not very far from the ground-state configuration.

## B. SOMMERFELD EXPANSION (INTEGRATION TECHNIQUE)

(1) Sommerfeld expansion

$$\int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon \approx \int_0^\mu g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu)$$

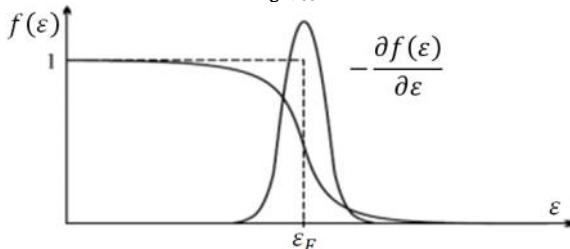
PROOF:

1. Integration by parts

Let  $g(\varepsilon) = \frac{dG(\varepsilon)}{d\varepsilon} = G'(\varepsilon)$  and  $G(E) = \int_0^E g(\varepsilon) d\varepsilon$

$$\begin{aligned} I &= \int_0^\infty f(\varepsilon)g(\varepsilon) d\varepsilon \\ &= \int_0^\infty f(\varepsilon) \frac{dG(\varepsilon)}{d\varepsilon} d\varepsilon \\ &= f(\varepsilon)G(\varepsilon) \Big|_0^\infty - \int_0^\infty \frac{\partial f(\varepsilon)}{\partial \varepsilon} G(\varepsilon) d\varepsilon \\ &= \int_0^\infty \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) G(\varepsilon) d\varepsilon \end{aligned}$$

where  $G(0) = 0$  and  $\lim_{\varepsilon \rightarrow \infty} f(\varepsilon)G(\varepsilon) \rightarrow 0$



2. If the function  $G(\varepsilon)$  is slowly varying compared to  $\partial f / \partial \varepsilon$  in the region  $\varepsilon \approx \mu$ , we can expand  $G(\varepsilon)$  in Taylor series as follows:

$$G(\varepsilon) = G(\mu) + (\varepsilon - \mu)G'(\mu) + \frac{1}{2}(\varepsilon - \mu)^2 G''(\mu) + \dots$$

$$\begin{aligned} I &= \int_0^\infty \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \left[ G(\mu) + (\varepsilon - \mu)G'(\mu) + \frac{1}{2}(\varepsilon - \mu)^2 G''(\mu) \right] d\varepsilon \\ &= G(\mu) \int_0^\infty \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) d\varepsilon + G'(\mu) \int_0^\infty \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) (\varepsilon - \mu) d\varepsilon \\ &\quad + \frac{1}{2} G''(\mu) \int_0^\infty \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) (\varepsilon - \mu)^2 d\varepsilon \end{aligned}$$

Let  $x = \beta(\varepsilon - \mu)$

$$\text{Since } \frac{\partial f(\varepsilon)}{\partial \varepsilon} = \frac{\beta e^{\beta(\varepsilon-\mu)}}{(e^{\beta(\varepsilon-\mu)} + 1)^2}$$

$$\begin{aligned}
\int_0^\infty \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) (\varepsilon - \mu)^z d\varepsilon &= \int_0^\infty \frac{\beta e^{\beta(\varepsilon-\mu)}}{(e^{\beta(\varepsilon-\mu)} + 1)^2} (\varepsilon - \mu)^z d\varepsilon \\
&= \frac{1}{\beta^z} \int_{-\mu/k_B T}^\infty \frac{x^z e^x}{e^{2x} + 2e^x + 1} dx \\
&= (k_B T)^z \int_{-\mu/k_B T}^\infty \frac{x^z}{(e^x + 1)(e^{-x} + 1)} dx \\
&\approx (k_B T)^z \int_{-\infty}^\infty \frac{x^z}{(e^x + 1)(e^{-x} + 1)} dx
\end{aligned}$$

where in metal,  $k_B T \ll \mu$ , the lower limit of the integral can be replaced by  $-\infty$ .

$$\begin{aligned}
I &= G(\mu) \underbrace{\int_0^\infty \delta(\varepsilon) d\varepsilon}_{=1} + (k_B T) G'(\mu) \underbrace{\int_{-\infty}^\infty \frac{x}{(e^x + 1)(e^{-x} + 1)} dx}_{=0} \\
&\quad + \frac{1}{2} (k_B T)^2 G''(\mu) \underbrace{\int_{-\infty}^\infty \frac{x^2}{(e^x + 1)(e^{-x} + 1)} dx}_{=\frac{\pi^2}{3}} + \dots \\
&\approx G(\mu) + \frac{\pi^2}{6} (k_B T)^2 G''(\mu) \\
&= \int_0^\mu g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu)
\end{aligned}$$

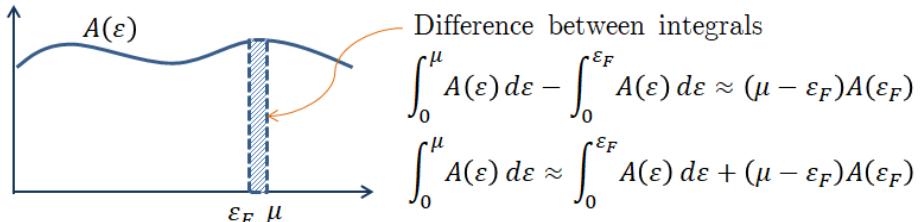
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### C. ELECTRONIC SPECIFIC HEAT $C_v = \frac{\partial U}{\partial T}$

(1) Internal energy

$$\begin{aligned}
U &= \sum_k \varepsilon_k n_k \\
&= \frac{\mathcal{V}}{(2\pi)^3} \int \varepsilon_k n_k d^3k \\
&= \mathcal{V} \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon \\
&= \mathcal{V} \int_0^\mu \varepsilon g(\varepsilon) d\varepsilon + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 \left. \frac{d(\varepsilon g(\varepsilon))}{d\varepsilon} \right|_{E_F} \\
&= \mathcal{V} \int_0^\mu \varepsilon g(\varepsilon) d\varepsilon + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 \varepsilon_F g'(\varepsilon_F)
\end{aligned}$$

If a function  $A(\varepsilon)$  is slowly varying around  $\mu$



$$\int_0^\mu \varepsilon g(\varepsilon) d\varepsilon \approx \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + (\mu - \varepsilon_F) \varepsilon_F g(\varepsilon_F)$$

$$\begin{aligned}
U &\approx \mathcal{V} \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \mathcal{V} (\mu - \varepsilon_F) \varepsilon_F g(\varepsilon_F) + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) \\
&\quad + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 \varepsilon_F g'(\varepsilon_F)
\end{aligned}$$

Using the identity

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

**PROOF:**

$$\begin{aligned}
N &= \mathcal{V} \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon \\
&\approx \mathcal{V} \int_0^\mu g(\varepsilon) d\varepsilon + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g'(\mu) \\
&\approx \mathcal{V} \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon + \mathcal{V} (\mu - \varepsilon_F) g(\varepsilon_F) + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \\
&= N + \mathcal{V} (\mu - \varepsilon_F) g(\varepsilon_F) + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F)
\end{aligned}$$

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

The internal energy becomes

$$\begin{aligned} U &= \mathcal{V} \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon - \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 \varepsilon_F g'(\varepsilon_F) + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) \\ &\quad + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 \varepsilon_F g'(\varepsilon_F) \\ &= \mathcal{V} \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) \end{aligned}$$

(2) The density of states of a metal

$$\begin{aligned} g(\varepsilon) &= \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} \\ U &= \mathcal{V} \int_0^{\varepsilon_F} \varepsilon \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} d\varepsilon + \mathcal{V} \frac{\pi^2}{6} (k_B T)^2 \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} \\ &= \frac{\mathcal{V}}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{5/2} + \frac{\mathcal{V}}{12} (k_B T)^2 \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} \end{aligned}$$

(3) The electronic specific heat is

$$C_v = \frac{\partial U}{\partial T} = \frac{\mathcal{V}}{6} k_B^2 T \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} = \gamma T$$

where

$$\begin{aligned} \gamma &= \frac{\mathcal{V}}{6} k_B^2 \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} \\ &= \frac{\mathcal{V}}{6} k_B^2 \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{\hbar k_F}{\sqrt{2m}} \\ &= \frac{\mathcal{V}}{6} k_B^2 \left( \frac{2m}{\hbar^2} \right) k_F \\ &= \frac{\mathcal{V}}{6} k_B^2 \left( \frac{2m}{\hbar^2 k_F^2} \right) k_F^3 \end{aligned}$$

Since

$$k_F^3 = \left( \frac{3\pi^2 N}{\mathcal{V}} \right)$$

$$\gamma = \frac{\mathcal{V}}{6} k_B^2 \left( \frac{2m}{\hbar^2 k_F^2} \right) \left( \frac{3\pi^2 N}{\mathcal{V}} \right) = \frac{N\pi^2}{2} \frac{k_B^2}{\epsilon_F} = \frac{N\pi^2}{2} \frac{k_B^2}{k_B T_F} = \frac{N\pi^2 k_B}{2T_F}$$

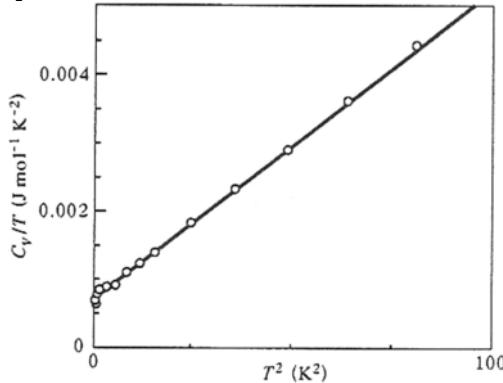
- (4) The total specific heat of a metal at low temperature takes the form  
 $C_v = \gamma T + \alpha T^3$

where  $\gamma T$  is the electronic specific heat and  $\alpha T^3$  is due to lattice vibrations. As the temperature is reduced,  $\alpha T^3$  approaches zero far more rapidly than the electronic specific heat.

### EXAMPLES:

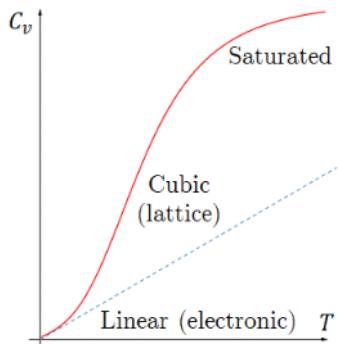
1. Low temperature specific heat of copper

$$\frac{C_v}{T} = \gamma + \alpha T^2$$

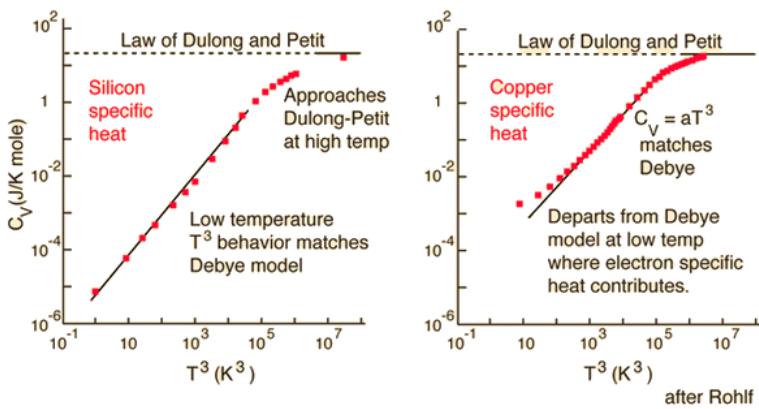


2. Explain the following figure

- (a) Specific heat of metal



- (b) Specific heat of insulator & metal



OS:

James William Rohlf, Modern Physics from  $\alpha$  to  $Z^0$ , Wiley, 1994.

Strong experimental deviations from this number are observed for, for instance, Nb, Fe, Mn, Bi, and Sb.

## D. ENTROPY AND FREE ENERGY

### (1) Entropy

$$\begin{aligned}
 \Omega &= -k_B T \ln Z \\
 &= -k_B T \ln \prod_k \left[ 1 + e^{-\beta(\varepsilon_k - \mu)} \right] \\
 &= -k_B T \sum_k \ln \left( 1 + e^{-\beta(\varepsilon_k - \mu)} \right) \\
 &= k_B T \sum_k \ln \left( \frac{1}{1 + e^{-\beta(\varepsilon_k - \mu)}} \right) \\
 &= k_B T \sum_k \ln \left( 1 - \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1} \right) \\
 &= k_B T \sum_k \ln(1 - \langle n_k \rangle)
 \end{aligned}$$

$$\begin{aligned}
S &= -\frac{\partial \Omega}{\partial T} \\
&= -k_B \sum_k \ln(1 - \langle n_k \rangle) + k_B T \sum_k \frac{1}{1 - \langle n_k \rangle} \frac{\partial}{\partial T} \langle n_k \rangle \\
&= -k_B \sum_k \ln(1 - \langle n_k \rangle) + k_B \sum_k \langle n_k \rangle \ln\left(\frac{1 - \langle n_k \rangle}{\langle n_k \rangle}\right) \\
&= -k_B \sum_k \left[ (1 - \langle n_k \rangle) \ln(1 - \langle n_k \rangle) + \langle n_k \rangle \ln\langle n_k \rangle \right]
\end{aligned}$$

OS:

$$\begin{aligned}
\frac{1}{1 - \langle n_k \rangle} &= \frac{(1 + e^{\beta(\varepsilon_k - \mu)})}{e^{\beta(\varepsilon_k - \mu)}} \\
\frac{\partial}{\partial T} \langle n_k \rangle &= \frac{\partial}{\partial T} (1 + e^{\beta(\varepsilon_k - \mu)})^{-1} = -\frac{\beta(\varepsilon_k - \mu) e^{\beta(\varepsilon_k - \mu)}}{T (1 + e^{\beta(\varepsilon_k - \mu)})^2} \\
\frac{1}{1 - \langle n_k \rangle} \frac{\partial}{\partial T} \langle n_k \rangle &= -\frac{(1 + e^{\beta(\varepsilon_k - \mu)})}{e^{\beta(\varepsilon_k - \mu)}} \frac{\beta(\varepsilon_k - \mu) e^{\beta(\varepsilon_k - \mu)}}{T (1 + e^{\beta(\varepsilon_k - \mu)})^2} \\
&= -\frac{\beta(\varepsilon_k - \mu)}{T} \langle n_k \rangle
\end{aligned}$$

and

$$\ln \frac{1 - \langle n_k \rangle}{\langle n_k \rangle} = \ln \frac{e^{\beta(\varepsilon_k - \mu)}}{\frac{1 + e^{\beta(\varepsilon_k - \mu)}}{1 + e^{\beta(\varepsilon_k - \mu)}}} = \ln e^{\beta(\varepsilon_k - \mu)} = \beta(\varepsilon_k - \mu)$$

(2) Free energy

$$\begin{aligned}
F &= U - TS \\
&= \sum_k \varepsilon_k \langle n_k \rangle + k_B T \sum_k \left[ (1 - \langle n_k \rangle) \ln(1 - \langle n_k \rangle) + \langle n_k \rangle \ln\langle n_k \rangle \right] \\
&= N\mu + k_B T \sum_k \ln(1 - \langle n_k \rangle) \\
&= N\mu - k_B T \sum_k \ln(1 + e^{-\beta(\varepsilon_k - \mu)})
\end{aligned}$$

# 5-5 Compressibility and Susceptibility

Tuesday, December 20, 2011 8:30 PM

## A. COMPRESSIBILITY

- (1) The compressibility  $\kappa_T$  is defined by

$$\frac{1}{\kappa_T} = -\mathcal{V} \left( \frac{\partial P}{\partial \mathcal{V}} \right)_{T,\mu} = \mathcal{V} \left( \frac{\partial^2 U}{\partial \mathcal{V}^2} \right)_{T,\mu}$$

where the hydrostatic pressure  $P$  of a Fermi gas is

$$P = - \left( \frac{\partial U}{\partial \mathcal{V}} \right)_{T,\mu} \quad \text{where } U = \sum_k \varepsilon_k n_k$$

- (2) At  $T = 0$

$$U = \sum_k \varepsilon_k n_k = \sum_{k \leq k_F} \varepsilon_k$$

Since

$$\begin{aligned} \varepsilon_k &= \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \frac{4\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{2m} \frac{4\pi^2 n^2}{\mathcal{V}^{2/3}} \\ \frac{\partial \varepsilon_k}{\partial \mathcal{V}} &= \frac{\partial}{\partial \mathcal{V}} \left( \frac{\hbar^2}{2m} \frac{4\pi^2 n^2}{\mathcal{V}^{2/3}} \right) = \frac{\hbar^2}{2m} 4\pi^2 n^2 \left( -\frac{2}{3} \frac{1}{\mathcal{V}^{5/3}} \right) = -\frac{2\varepsilon_k}{3\mathcal{V}} \end{aligned}$$

The hydrostatic pressure is

$$\begin{aligned} P &= -\frac{\partial}{\partial \mathcal{V}} \sum_{k \leq k_F} \varepsilon_k \\ &= -\sum_{k \leq k_F} \left( -\frac{2\varepsilon_k}{3\mathcal{V}} \right) \\ &= \frac{2}{3} \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon \\ &= \frac{2}{3} \int_0^{\varepsilon_F} \varepsilon \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} d\varepsilon \\ &= \frac{2}{3} \times \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \times \frac{2}{5} \varepsilon_F^{5/2} \end{aligned}$$

Since

$$\frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} = \frac{k_F^3}{2\pi^2} \left( \frac{2m}{\hbar^2 k_F^2} \right)^{3/2} = \frac{3}{2} n \varepsilon_F^{-3/2}$$

$$P = \frac{2}{3} \times \frac{3}{2} n \varepsilon_F^{-3/2} \times \frac{2}{5} \varepsilon_F^{5/2} = \frac{2n\varepsilon_F}{5}$$

The compressibility is

$$\begin{aligned} \frac{1}{\kappa_T} &= -\mathcal{V} \left( \frac{\partial P}{\partial \mathcal{V}} \right)_{T,\mu} \\ &= -\mathcal{V} \frac{\partial}{\partial \mathcal{V}} \sum_{k \leq k_F} \frac{2\varepsilon_k}{3\mathcal{V}} \\ &= -\mathcal{V} \sum_{k \leq k_F} \frac{2}{3} \left( -\frac{\varepsilon_k}{\mathcal{V}^2} - \frac{1}{\mathcal{V}} \frac{2\varepsilon_k}{3\mathcal{V}} \right) \\ &= \frac{5}{3} \sum_{k \leq k_F} \frac{2\varepsilon_k}{3\mathcal{V}} \\ &= \frac{5}{3} \times \frac{2n\varepsilon_F}{5} \\ &= \frac{2n\varepsilon_F}{3} \end{aligned}$$

Alternative method:

$$\frac{1}{\kappa_T} = \mathcal{V} \left( \frac{\partial^2 U}{\partial \mathcal{V}^2} \right)_{T,\mu} = \mathcal{V} \sum_{k \leq k_F} \frac{\partial^2 \varepsilon_k}{\partial \mathcal{V}^2}$$

Since  $\varepsilon_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \frac{4\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{2m} \frac{4\pi^2 n^2}{\mathcal{V}^{2/3}}$

$$\frac{\partial \varepsilon_k}{\partial \mathcal{V}} = \frac{\partial}{\partial \mathcal{V}} \left( \frac{\hbar^2}{2m} \frac{4\pi^2 n^2}{\mathcal{V}^{2/3}} \right) = \frac{\hbar^2}{2m} 4\pi^2 n^2 \left( -\frac{2}{3} \frac{1}{\mathcal{V}^{5/3}} \right) = -\frac{2\varepsilon_k}{3\mathcal{V}}$$

$$\frac{\partial^2 \varepsilon_k}{\partial \mathcal{V}^2} = \frac{\partial}{\partial \mathcal{V}} \left( -\frac{2\varepsilon_k}{3\mathcal{V}} \right) = \frac{10\varepsilon_k}{9\mathcal{V}^2}$$

$$\frac{1}{\kappa_T} = \mathcal{V} \sum_{k \leq k_F} \frac{10\varepsilon_k}{9\mathcal{V}^2} = \frac{5}{3} \sum_{k \leq k_F} \frac{3\varepsilon_k}{2\mathcal{V}} = \frac{2n\varepsilon_F}{3}$$

- (3) Sound waves in solids are composed of compression waves. The velocity of sound in solid is given by

$$s = \frac{1}{\sqrt{\kappa_T \rho}} \text{ and } \rho = \frac{nM}{z}$$

where  $\rho$  is the mass density,  $M$  is the ionic mass and  $z$  is the number of electrons per atom.

The velocity of sound in a metal at  $T = 0$  is

$$s = \sqrt{\frac{2n\varepsilon_F}{\frac{3}{z}M}} = \sqrt{\frac{2n\frac{mv_F^2}{2}}{\frac{3}{z}M}} = \sqrt{\frac{zm}{3M}} v_F$$

## B. SUSCEPTIBILITY

- (1) The magnetization is defined as

$$\vec{M} = \frac{N}{V} \vec{m} = -\frac{1}{V} \left( \frac{\partial F}{\partial \vec{B}} \right)_T$$

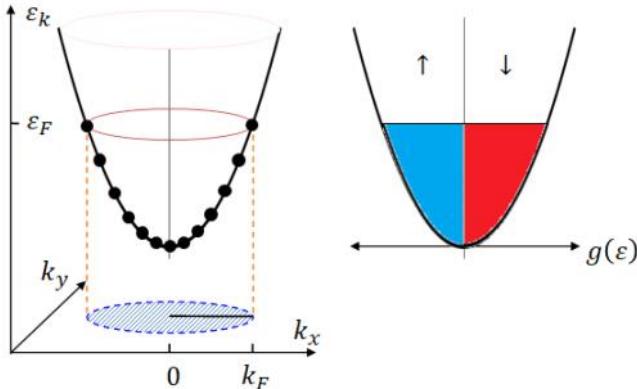
where  $\vec{m}$  is the magnetic moment and  $\vec{B}$  is the external field.

The susceptibility is

$$\chi = \mu_0 \frac{\partial \vec{M}}{\partial \vec{B}}$$

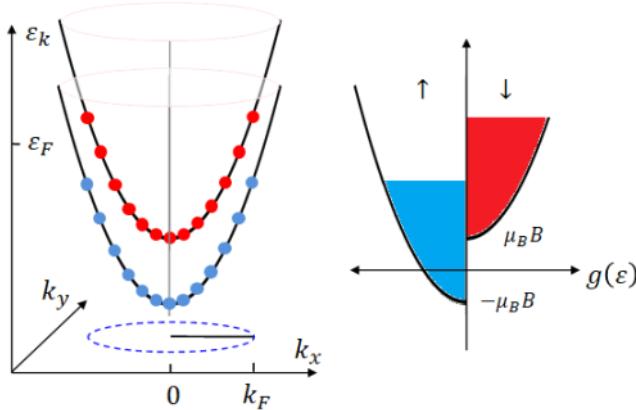
- (2) Para-magnetism: spin effect (Pauli, 1925)

$$B = 0$$

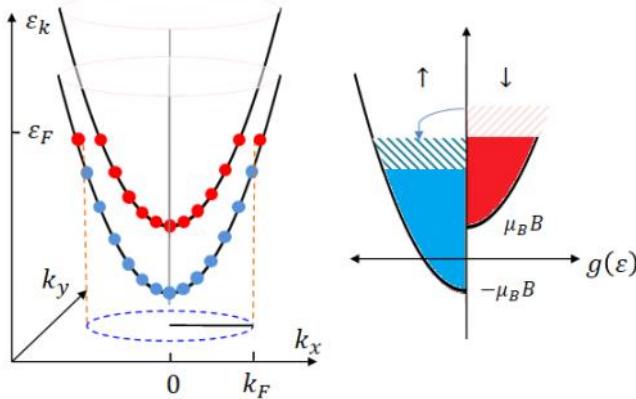


$$N_\uparrow = N_\downarrow$$

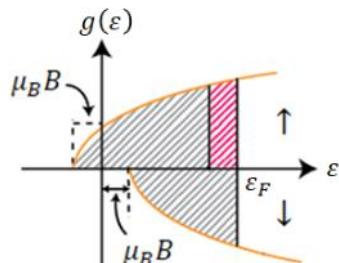
Apply an external field  $\vec{B}$ , energy levels shift



At equilibrium, electrons in the shaded region (up spin) go into lower energy states (down spin) and flip spins.



The number of down spins is larger than the number of up spins. Overall, this imbalance causes an overall magnetization.



At  $T = 0$

$$N_{\uparrow} = \frac{1}{2} \sum_{k \leq k_F} n_k = \frac{\mathcal{V}}{2} \int_{-\mu_B B}^{\epsilon_F} g(\epsilon + \mu_B B) d\epsilon$$

$$\begin{aligned}
N_{\downarrow} &= \frac{1}{2} \sum_{k \leq k_F} n_k = \frac{\mathcal{V}}{2} \int_{\mu_B B}^{\varepsilon_F} g(\varepsilon - \mu_B B) d\varepsilon \\
M &= \frac{(N_{\uparrow} - N_{\downarrow})}{\mathcal{V}} \mu_B \\
&= \frac{\mu_B}{2} \left( \int_{-\mu_B B}^{\varepsilon_F} g(\varepsilon + \mu_B B) d\varepsilon - \int_{\mu_B B}^{\varepsilon_F} g(\varepsilon - \mu_B B) d\varepsilon \right) \\
&= \frac{\mu_B}{2} \left( \int_0^{\varepsilon_F + \mu_B B} g(\varepsilon) d\varepsilon - \int_0^{\varepsilon_F - \mu_B B} g(\varepsilon) d\varepsilon \right) \\
&= \frac{\mu_B}{2} \int_{\varepsilon_F - \mu_B B}^{\varepsilon_F + \mu_B B} g(\varepsilon) d\varepsilon \\
&= \frac{\mu_B}{2} 2\mu_B B g(\varepsilon_F) \\
&= \mu_B^2 B g(\varepsilon_F) \\
g(\varepsilon_F) &= \frac{k_F^3}{2\pi^2 \varepsilon_F} = \frac{3n}{2\varepsilon_F} \\
M &= \frac{3n\mu_B^2 B}{2\varepsilon_F} \\
\chi &= \mu_0 \frac{\partial M}{\partial B} = \frac{3n\mu_0\mu_B^2}{2\varepsilon_F} > 0 \dots \text{paramagnetism}
\end{aligned}$$

(3) Diamagnetism: orbital effect (Landau, 1930)

In the presence of a magnetic field  $\vec{B} = B\hat{z}$

Since  $\vec{B} = \nabla \times \vec{A}$ ,  $\vec{A} = (0, Bx, 0)$

$$\begin{aligned}
\hat{H} &= \frac{1}{2m} \left( \hat{p} + \frac{e}{c} \vec{A} \right)^2 \\
&= \frac{1}{2m} \left( \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 + \frac{2eB}{c} \hat{p}_y \hat{x} + \frac{e^2 B^2}{c^2} \hat{x}^2 \right) \\
&= \frac{\hat{p}_x^2}{2m} + \frac{\left( \hat{p}_y + \frac{eB}{c} \hat{x} \right)^2}{2m} + \frac{\hat{p}_z^2}{2m} \\
&= \frac{\hat{p}_x^2}{2m} + \frac{e^2 B^2}{2mc^2} \left( \hat{x} + \frac{c\hat{p}_y}{eB} \right)^2 + \frac{\hat{p}_z^2}{2m}
\end{aligned}$$

Let the cyclotron frequency (Larmor frequency)

$$\omega_c = \frac{eB}{mc}$$

Since  $[\hat{p}_y, \hat{H}] = [\hat{p}_z, \hat{H}] = 0$ ,  $\hat{p}_y$  and  $\hat{p}_z$  can be substituted by their eigenvalues  $\hbar k_y$  and  $\hbar k_z$ .

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2 \left( \hat{x} + \frac{\hbar ck_y}{eB} \right)^2 + \frac{\hbar^2 k_z^2}{2m} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2 (\hat{x} + l_B^2 k_y)^2 + \frac{\hbar^2 k_z^2}{2m}$$

where  $l_B^2 = \hbar c/eB$  is the magnetic length.

The Hamiltonian describes the harmonic oscillator with its well centered at  $x_0$  and the eigenenergies are

$$\varepsilon_{nk} = \hbar\omega_c \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m}$$

The number of states in the  $n$ -th Landau level with  $z$ -component of the momentum  $k_z$  is given by

$$N(k) = \frac{\mathcal{V}}{2\pi l_B^2} \frac{k_z}{2\pi} = \frac{\mathcal{V} e B k_z}{(2\pi)^2 \hbar c} = \frac{\mathcal{V} m \omega_c k_z}{4\pi^2 \hbar}$$

$$\text{Since } k_z = \frac{\sqrt{2m}}{\hbar} \sqrt{\varepsilon_{nk} - \hbar\omega_c \left( n + \frac{1}{2} \right)}$$

$$N(\varepsilon) = \frac{\mathcal{V} m \omega_c \sqrt{2m}}{4\pi^2 \hbar} \frac{1}{\hbar} \sqrt{\varepsilon - \hbar\omega_c \left( n + \frac{1}{2} \right)} = \frac{\mathcal{V} (2m)^{3/2} \omega_c}{8\pi^2 \hbar^2} \sqrt{\varepsilon - \hbar\omega_c \left( n + \frac{1}{2} \right)}$$

The density of states, with accounting for the spin degeneracy and for the positive and the negative  $k_z$  values, is

$$g_n(\varepsilon) = \sum_{\substack{\text{spin} \\ \pm k_z}} \times \frac{1}{2} \times \frac{1}{\mathcal{V}} \frac{dN(\varepsilon)}{d\varepsilon} = \frac{(2m)^{3/2} \omega_c}{4\pi^2 \hbar^2} \frac{1}{\sqrt{\varepsilon - \hbar\omega_c(n + 1/2)}}$$

The free energy is

$$\begin{aligned} F &= N\mu - k_B T \sum_{nk} \ln \left( 1 + e^{-(\varepsilon_{nk} - \mu)/k_B T} \right) \\ &= N\mu - k_B T \mathcal{V} \sum_{n=0}^{\infty} \int_{\hbar\omega_c(n+1/2)}^{\infty} \ln \left( 1 + e^{-(\varepsilon_n - \mu)/k_B T} \right) g_n(\varepsilon) d\varepsilon \\ &= N\mu - k_B T \mathcal{V} \frac{(2m)^{3/2} \omega_c}{4\pi^2 \hbar^2} \sum_{n=0}^{\infty} \int_{\hbar\omega_c(n+1/2)}^{\infty} \frac{\ln \left( 1 + e^{-(\varepsilon_n - \mu)/k_B T} \right)}{\sqrt{\varepsilon - \hbar\omega_c(n + 1/2)}} d\varepsilon \end{aligned}$$

integral by parts

$$= N\mu - \mathcal{V} \frac{(2m)^{3/2} \omega_c}{2\pi^2 \hbar^2} \sum_{n=0}^{\infty} \int_{\hbar\omega_c(n+1/2)}^{\infty} \frac{\sqrt{\varepsilon - \hbar\omega_c(n + 1/2)}}{1 + e^{-(\varepsilon - \mu)/k_B T}} d\varepsilon$$

At  $T = 0$

$$\Rightarrow \begin{cases} 1 + e^{-(\varepsilon - \mu)/k_B T} = 1 \\ \mu = \varepsilon_F \end{cases}$$

$$F = N\varepsilon_F - \mathcal{V} \frac{(2m)^{3/2}\omega_c}{2\pi^2\hbar^2} \sum_{n=0}^{n_0} \int_{\hbar\omega_c(n+1/2)}^{\varepsilon_F} \sqrt{\varepsilon - \hbar\omega_c(n+1/2)} d\varepsilon$$

$$= N\varepsilon_F - \mathcal{V} \frac{(2m)^{3/2}\omega_c}{3\pi^2\hbar^2} \sum_{n=0}^{n_0} (\varepsilon_F - \hbar\omega_c(n+1/2))^{3/2}$$

Let  $x = \varepsilon_F/\hbar\omega_c$

$$F = N\varepsilon_F - \mathcal{V} \frac{(2\hbar\omega_c m)^{3/2}\omega_c}{3\pi^2\hbar^2} \sum_{n=0}^{n_0} (x - n - 1/2)^{3/2}$$

For large  $n_0$ , we use the Euler-Maclaurin formula

$$\sum_{n=0}^{n_0} (x - n - 1/2)^{3/2} \approx \frac{2}{5}x^{5/2} - \frac{1}{16}x^{1/2}$$

$$F = N\varepsilon_F - \mathcal{V} \frac{2(2m)^{3/2}\varepsilon_F^{5/2}}{15\pi^2\hbar^3} + \mathcal{V} \frac{(2m)^{3/2}\omega_c^2\varepsilon_F^{1/2}}{48\pi^2\hbar}$$

$$M = -\frac{1}{\mathcal{V}} \frac{\partial F}{\partial B} = -\frac{(2m)^{3/2}e^2\varepsilon_F^{1/2}}{24\pi^2\hbar m^2 c^2} B = -\frac{1}{3} \left( \frac{3n\mu_B^2}{2\varepsilon_F} \right) B$$

$$\chi_{\text{Landou}} = \mu_0 \frac{\partial M}{\partial B} = -\frac{n\mu_0\mu_B^2}{2\varepsilon_F} = -\frac{1}{3} \chi_{\text{Pauli}} < 0 \dots \text{diamagnetism}$$

(4) The total susceptibility of a metal is

$$\chi = \chi_{\text{Pauli}} + \chi_{\text{Landou}} = \chi_{\text{Pauli}} - \frac{1}{3} \chi_{\text{Pauli}} = \frac{2}{3} \chi_{\text{Pauli}} = \frac{n\mu_0\mu_B^2}{\varepsilon_F}$$

# 6-1 Boltzmann Equation

Tuesday, December 20, 2011 8:29 PM

## A. LORENTZ THEORY

- (1) Assume electrons, in equilibrium state, are followed Maxwell velocity distribution function,

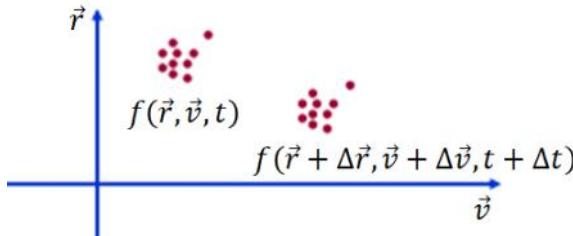
$$f_0(\vec{r}, \vec{v}) = n \left( \frac{m}{2\pi k_B T(\vec{r})} \right)^{3/2} e^{-mv^2/2k_B T(\vec{r})}$$

where  $T(\vec{r})$  depend on position. When an external field is applied, the equilibrium distribution function  $f_0(\vec{r}, \vec{v})$  becomes the non-equilibrium distribution function  $f(\vec{r}, \vec{v}, t)$ .

- (2) Consider the rate of change between final and initial distribution function

$$\frac{df}{dt} = \frac{f(\vec{r} + \Delta\vec{r}, \vec{v} + \Delta\vec{v}, t + \Delta t) - f(\vec{r}, \vec{v}, t)}{\Delta t}$$

If no collisions occurred between the electrons,

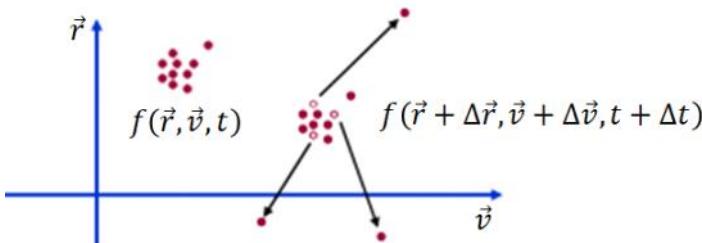


According to Liouville's theorem,

$$f(\vec{r} + \Delta\vec{r}, \vec{v} + \Delta\vec{v}, t + \Delta t) = f(\vec{r}, \vec{v}, t)$$

$$\frac{df}{dt} = 0$$

If collisions take place between the electrons,



$$f(\vec{r} + \Delta\vec{r}, \vec{v} + \Delta\vec{v}, t + \Delta t) \neq f(\vec{r}, \vec{v}, t)$$

$$\frac{df}{dt} \equiv \mathcal{J}_{\text{coll}}$$

is called collision integral.

- (3) Suppose that collisions relax the non-equilibrium distribution back to the equilibrium distribution with a single time constant  $\tau$

$$\begin{aligned}\mathcal{J}_{\text{coll}} &= \frac{\Delta f}{\Delta t} = \frac{f_0 - f}{\tau} = -\frac{f - f_0}{\tau} \\ \Rightarrow \frac{df}{dt} &= \frac{\partial f}{\partial \vec{r}} \cdot \frac{\partial \vec{r}}{\partial t} + \frac{\partial f}{\partial \vec{v}} \cdot \frac{\partial \vec{v}}{\partial t} + \frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}\end{aligned}$$

$$\text{Since } \frac{\partial \vec{r}}{\partial t} = \vec{v} \text{ and } \frac{\partial \vec{v}}{\partial t} = \vec{F}$$

The Boltzmann transport equation can be written as

$$\vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m} \cdot \frac{\partial f}{\partial \vec{v}} + \frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}$$

When an electron moving in an electric field and a magnetic field, the Lorentz force is

$$\begin{aligned}\vec{F} &= -e\vec{E} - \frac{e}{c}\vec{v} \times \vec{B} \\ \Rightarrow \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} - \frac{e}{m} \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \cdot \frac{\partial f}{\partial \vec{v}} + \frac{\partial f}{\partial t} &= -\frac{f - f_0}{\tau}\end{aligned}$$

- (4) Assume an applied external field is small and the non-equilibrium distribution function is a small deviation from the equilibrium distribution function,  $f = f_0 + \delta f$ .

$$\underbrace{\vec{v} \cdot \frac{\partial}{\partial \vec{r}} (f_0 + \delta f)}_{\textcircled{1}} - \underbrace{\frac{e}{m} \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \cdot \frac{\partial}{\partial \vec{v}} (f_0 + \delta f)}_{\textcircled{2}} + \underbrace{\frac{\partial}{\partial t} (f_0 + \delta f)}_{\textcircled{3}} = -\frac{\delta f}{\tau}$$

The equation above is a non-linear equation. We would like to make a linearized equation.

Case ① (temperature effect):

$$\frac{\partial}{\partial \vec{r}}(f_0 + \delta f) = \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial \vec{r}} + \frac{\partial \delta f}{\partial T} \frac{\partial T}{\partial \vec{r}}$$

Since  $\frac{\partial \delta f}{\partial T}$  of the second term is smaller compared to the first term, we ignore the term and obtain

$$\frac{\partial}{\partial \vec{r}}(f_0 + \delta f) \approx \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial \vec{r}} = \frac{\partial f_0}{\partial T} \nabla T$$

Case ② (electric & magnetic field):

$$-\frac{e}{m} \vec{E} \cdot \frac{\partial}{\partial \vec{v}}(f_0 + \delta f) = -\frac{e}{m} \vec{E} \cdot \frac{\partial f_0}{\partial \vec{v}} - \frac{e}{m} \vec{E} \cdot \frac{\partial \delta f}{\partial \vec{v}}$$

Since  $\frac{\partial \delta f}{\partial \vec{v}}$  of the second term is smaller compared to the first term, we ignore the term and obtain

$$-\frac{e}{m} \vec{E} \cdot \frac{\partial}{\partial \vec{v}}(f_0 + \delta f) \approx -\frac{e}{m} \vec{E} \cdot \frac{\partial f_0}{\partial \vec{v}}$$

$$\begin{aligned} -\frac{e}{mc} \vec{v} \times \vec{B} \cdot \frac{\partial}{\partial \vec{v}}(f_0 + \delta f) &= -\frac{e}{mc} \vec{v} \times \vec{B} \cdot \frac{\partial f_0}{\partial \vec{v}} - \frac{e}{mc} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{v}} \\ &= \underbrace{-\frac{e}{mc} \vec{v} \times \vec{B} \cdot \hat{v} \frac{\partial f_0}{\partial v}}_{=0} - \frac{e}{mc} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{v}} \\ &= -\frac{e}{mc} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{v}} \end{aligned}$$

Case ③ (time-dependent):

$$\frac{\partial}{\partial t}(f_0 + \delta f) = \underbrace{\frac{\partial f_0}{\partial t}}_{=0} + \frac{\partial \delta f}{\partial t} = \frac{\partial \delta f}{\partial t}$$

The linearized Boltzmann equation is

$$\vec{v} \cdot \frac{\partial f_0}{\partial T} \nabla T - \frac{e}{m} \vec{E} \cdot \hat{v} \frac{\partial f_0}{\partial v} - \frac{e}{mc} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{v}} + \frac{\partial \delta f}{\partial t} = -\frac{\delta f}{\tau}$$

(5) The electric current density:

Let  $\nabla T = 0$ ,  $\vec{B} = 0$  and the steady state  $\frac{\partial \delta f}{\partial t} = 0$ :

$$-\frac{e}{m} \vec{E} \cdot \hat{v} \frac{\partial f_0}{\partial v} = -\frac{\delta f}{\tau} \Rightarrow \delta f = \frac{\tau e}{m} \frac{\partial f_0}{\partial v} \hat{v} \cdot \vec{E}$$

$$\vec{j}_e = \int (-e) \vec{v} \delta f d^3 v = \int (-e) \vec{v} \frac{\tau e}{m} \frac{\partial f_0}{\partial v} \hat{v} \cdot \vec{E} d^3 v = -\underbrace{\frac{\tau e^2}{m} \int \vec{v} \hat{v} \frac{\partial f_0}{\partial v} d^3 v}_{\vec{\sigma}} \cdot \vec{E}$$

(6) The thermal current density:

Let  $\vec{E} = 0$ ,  $\vec{B} = 0$  and the steady state  $\frac{\partial \delta f}{\partial t} = 0$ :

$$\vec{v} \cdot \frac{\partial f_0}{\partial T} \nabla T = -\frac{\delta f}{\tau} \Rightarrow \delta f = -\tau \vec{v} \cdot \frac{\partial f_0}{\partial T} \nabla T$$

Since  $\frac{\partial f_0}{\partial T} = -\frac{3}{2} \frac{f_0}{T} + \frac{mv^2}{2k_B T} \frac{f_0}{T} = \left(\frac{3}{2} - \frac{\varepsilon}{k_B T}\right) f_0 \cdot \left(-\frac{1}{T}\right)$

$$\Rightarrow \delta f = -\tau \vec{v} \left(\frac{3}{2} - \frac{\varepsilon}{k_B T}\right) f_0 \cdot \left(-\frac{\nabla T}{T}\right) = \tau \vec{v} \left(\frac{\varepsilon}{k_B T} - \frac{3}{2}\right) f_0 \cdot \left(-\frac{\nabla T}{T}\right)$$

$$\vec{J}_Q = \int \varepsilon \vec{v} \delta f d^3 v = \underbrace{\int \varepsilon \vec{v} \tau \vec{v} \left(\frac{\varepsilon}{k_B T} - \frac{3}{2}\right) f_0 d^3 v}_{\bar{k}T} \cdot \left(-\frac{\nabla T}{T}\right)$$

## B. CONDUCTIVITY OF METALS

(1) Dc conductivity: Electrons in the constant electric field  $\vec{E} = E \hat{x}$ .

$$\bar{\sigma} = -\frac{\tau e^2}{m} \int \vec{v} \hat{v} \frac{\partial f_0}{\partial v} d^3 v$$

The diagonal electric conductivity is

$$\begin{aligned} \sigma &= -\frac{\tau e^2}{m} \int v \cos \theta \cos \theta \frac{\partial f_0}{\partial v} v^2 dv \sin \theta d\theta d\phi \\ &= -\frac{\tau e^2}{m} \underbrace{\int v^3 \frac{\partial f_0}{\partial v} dv}_{-\frac{3n}{4\pi}} \underbrace{\int_0^\pi \cos^2 \theta \sin \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= \frac{n e^2 \tau}{m} \end{aligned}$$

OS:

Method 1: integral by parts

$$\begin{aligned} \int v^3 \frac{\partial f_0}{\partial v} dv &= -3 \int v^2 f_0 dv \\ &= -3n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int v^2 e^{-mv^2/2k_B T} dv \end{aligned}$$

$$\text{Since } \int_0^\infty x^{2n} e^{-\alpha x^2} dx = \frac{(2n-1)!!}{2(2\alpha)^n} \sqrt{\frac{\pi}{\alpha}}$$

$$\begin{aligned} \int v^3 \frac{\partial f_0}{\partial v} dv &= -3n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{1}{2} \left(\frac{2k_B T}{2m}\right) \sqrt{\frac{2\pi k_B T}{m}} \\ &= -\frac{3n}{4\pi} \end{aligned}$$

Method 2:

$$\begin{aligned}
\int v^3 \frac{\partial f_0}{\partial v} dv &= \int v^3 \left( -\frac{mv}{k_B T} \right) f_0 dv \\
&= \left( -\frac{m}{k_B T} \right) \int v^4 n \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv \\
&= \left( -\frac{m}{k_B T} \right) n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \frac{3}{2} \left( \frac{2k_B T}{2m} \right)^2 \sqrt{\frac{2\pi k_B T}{m}} \\
&= \left( -\frac{m}{k_B T} \right) \frac{3n}{4\pi} \left( \frac{k_B T}{m} \right) \\
&= -\frac{3n}{4\pi}
\end{aligned}$$

(2) Thermal conductivity: Electrons in a temperature gradient  $\nabla T = \frac{\partial T}{\partial x} \hat{x}$

$$\bar{\kappa}T = \int \varepsilon \vec{v} \cdot \tau \vec{v} \left( \frac{\varepsilon}{k_B T} - \frac{3}{2} \right) f_0 d^3 v$$

The diagonal electric conductivity is

$$\begin{aligned}
\kappa T &= \tau \int \varepsilon v \cos \theta v \cos \theta \left( \frac{\varepsilon}{k_B T} - \frac{3}{2} \right) f_0 v^2 dv \sin \theta d\theta d\phi \\
&= \tau \int \varepsilon v^4 \left( \frac{\varepsilon}{k_B T} - \frac{3}{2} \right) f_0 dv \underbrace{\int_0^{\pi} \cos^2 \theta \sin \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}
\end{aligned}$$

Since

$$\begin{aligned}
\frac{1}{k_B T} \int \varepsilon^2 v^4 f_0 dv &= \frac{m^2}{4k_B T} \int v^8 f_0 dv \\
&= \frac{m^2}{4k_B T} n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \frac{105}{2} \left( \frac{2k_B T}{2m} \right)^4 \sqrt{\frac{2\pi k_B T}{m}} \\
&= \frac{105}{16} \frac{n(k_B T)^2}{\pi m} \\
\frac{3}{2} \int \varepsilon v^4 f_0 dv &= \frac{3m}{4} \int v^6 f_0 dv \\
&= \frac{3m}{4} n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \frac{15}{2} \left( \frac{2k_B T}{2m} \right)^3 \sqrt{\frac{2\pi k_B T}{m}} \\
&= \frac{45}{16} \frac{n(k_B T)^2}{\pi m}
\end{aligned}$$

OS:

Use formula

$$\int_0^\infty x^{2n} e^{-\alpha x^2} dx = \frac{(2n-1)!!}{2(2\alpha)^n} \sqrt{\frac{\pi}{\alpha}}$$
$$\Rightarrow \int \varepsilon v^4 \left( \frac{\varepsilon}{k_B T} - \frac{3}{2} \right) f_0 dv = \left( \frac{105}{16} - \frac{45}{16} \right) \frac{n(k_B T)^2}{\pi m} = \frac{60}{16} \frac{n(k_B T)^2}{\pi m}$$

$$\kappa T = \tau \times \frac{60}{16} \frac{n(k_B T)^2}{\pi m} \times \frac{2}{3} \times 2\pi = \frac{5n\tau}{m} (k_B T)^2$$

Since  $\nabla T$  along  $x$ -axis only

$$\Rightarrow \kappa = \frac{1}{3} \left( \frac{5n\tau}{m} k_B^2 T \right)$$

(3) Wiedermann-Franz law

$$\frac{\kappa}{\sigma_0} = \frac{\frac{5n\tau}{3m} k_B^2 T}{\frac{ne^2\tau}{m}} = \frac{5}{3} \left( \frac{k_B}{e} \right)^2 T$$

$$L = \frac{\kappa}{\sigma_0 T} = \frac{5}{3} \left( \frac{k_B}{e} \right)^2 = 1.23 \times 10^{-8} \text{ W}\Omega/\text{K}^2$$

OS:

Hendrik Antoon Lorentz (1853-1928)

Since Drude's simple model gave some results that agree fairly well with experiment, Lorentz decided to use the full apparatus of kinetic theory to investigate the model more carefully. He did not succeed in improving on Drude's model, but he did make use of the Boltzmann distribution function and Boltzmann equation.

## 6-2 Relaxation Processes

Tuesday, May 14, 2013 4:08 PM

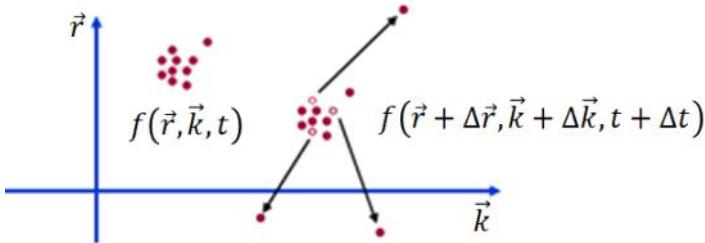
### A. COLLISION FUNCTION WITH FERMI-DIRAC DISTRIBUTION

- (1) In thermodynamic equilibrium, the local distribution function of quantum electrons is given by the Fermi-Dirac distribution.

$$f_0(\vec{r}, \vec{k}) = \frac{1}{e^{(\varepsilon(\vec{k}) - \mu(\vec{r}))/k_B T(\vec{r})} + 1}$$

where  $\mu(\vec{r})$  and  $T(\vec{r})$  depend on position.

- (2) In the presence of an external field, if collisions happened,



$$\mathcal{J}_{\text{coll}} = \frac{\partial \vec{r}}{\partial t} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \cdot \frac{\partial f}{\partial \vec{k}} + \frac{\partial f}{\partial t} = \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar} \cdot \frac{\partial f}{\partial \vec{k}} + \frac{\partial f}{\partial t}$$

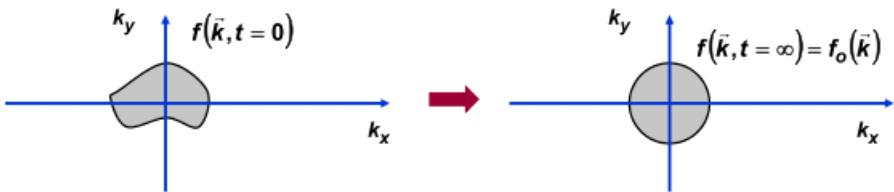
### B. RELAXATION PROCESSES

- (1) Relaxation time ansatz

If the external field creates a non-equilibrium distribution  $f(\vec{r}, \vec{k}, t)$ , and the field is then suddenly switched off, then from the moment  $t = 0$  of switching off

$$\mathcal{J}_{\text{coll}} = \underbrace{\vec{v} \cdot \frac{\partial f}{\partial \vec{r}}}_{=0} + \underbrace{\frac{\vec{F}}{\hbar} \cdot \frac{\partial f}{\partial \vec{k}}}_{=0} + \frac{\partial f}{\partial t}$$

Scattering must serve to drive the non-equilibrium distribution back towards thermal equilibrium at time  $t = \infty$  where  $f = f_0$ .



In the relaxation time approximation

$$\mathcal{J}_{\text{coll}} = -\frac{f - f_0}{\tau} \Rightarrow \frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}$$

The solution is

$$f = f_0 + [f(t=0) - f_0] e^{-t/\tau}$$

As  $t \rightarrow \infty, f \rightarrow f_0$

The relaxation time  $\tau$  is therefore the time constant with which the non-equilibrium distribution relaxes via scattering to the equilibrium state when the external perturbation is switched off.

## (2) Stationary non-equilibrium distribution

When the uniform external field is applied, the steady state distribution function is desired, i.e.,

$$\begin{aligned} \frac{\partial f}{\partial \vec{r}} &= 0 \text{ and } \frac{\partial f}{\partial t} = 0 \\ \Rightarrow \underbrace{\vec{v} \cdot \frac{\partial f}{\partial \vec{r}}}_{=0} + \frac{\vec{F}}{\hbar} \cdot \frac{\partial f}{\partial \vec{k}} + \underbrace{\frac{\partial f}{\partial t}}_{=0} &= \frac{\vec{F}}{\hbar} \cdot \frac{\partial f}{\partial \vec{k}} = -\frac{f - f_0}{\tau} \end{aligned}$$

Since  $\vec{F} = -\nabla(\hbar\phi)$

$$\begin{aligned} -\nabla\phi \cdot \frac{\partial f(\vec{k})}{\partial \vec{k}} &= -\frac{f - f_0}{\tau} \\ \Rightarrow \tau \nabla\phi \cdot \frac{\partial f(\vec{k})}{\partial \vec{k}} &= f(\vec{k}) - f_0(\vec{k}) \end{aligned}$$

$$\begin{aligned} f(\vec{k}) &= f_0(\vec{k}) + \tau \nabla\phi \cdot \frac{\partial f(\vec{k})}{\partial \vec{k}} \\ &= f_0(\vec{k}) + \tau \nabla\phi \cdot \frac{\partial}{\partial \vec{k}} \left[ f_0(\vec{k}) + \tau \nabla\phi \cdot \frac{\partial f(\vec{k})}{\partial \vec{k}} \right] \\ &= f_0(\vec{k}) + \tau \nabla\phi \cdot \frac{\partial f_0(\vec{k})}{\partial \vec{k}} + \tau^2 \left( \nabla\phi \cdot \frac{\partial}{\partial \vec{k}} \right) \left( \nabla\phi \cdot \frac{\partial f(\vec{k})}{\partial \vec{k}} \right) + \dots \end{aligned}$$

Assume the applied field is small, the small deviation from thermal

equilibrium is

$$f(\vec{k}) \approx f_0(\vec{k}) + \tau \nabla \phi \cdot \frac{\partial f_0(\vec{k})}{\partial \vec{k}} \approx f_0(\vec{k} + \tau \nabla \phi)$$

The stationary distribution can therefore be represented by a Fermi distribution shifted by  $\tau \nabla \phi$  from the equilibrium position.

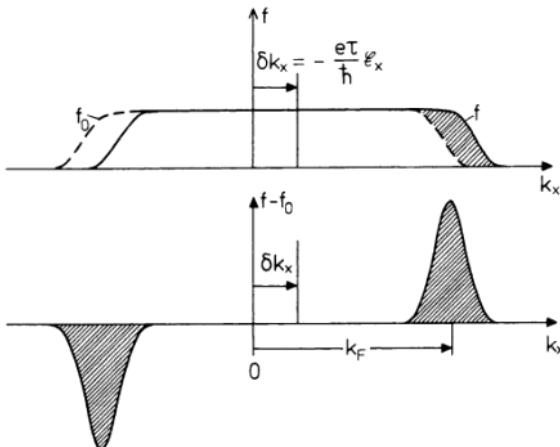
## EXAMPLES:

Ohmic conduction in solids

$$\vec{F} = -\nabla(\hbar\phi) = -e\vec{E} \Rightarrow \nabla\phi = \frac{e\vec{E}}{\hbar}$$

$$f(\vec{k}) = f_0(\vec{k}) + \tau \frac{e}{\hbar} \vec{E} \cdot \nabla f_0(\vec{k}) \approx f_0\left(\vec{k} + \tau \frac{e}{\hbar} \vec{E}\right) = f_0\left(\vec{k} - \delta\vec{k}\right)$$

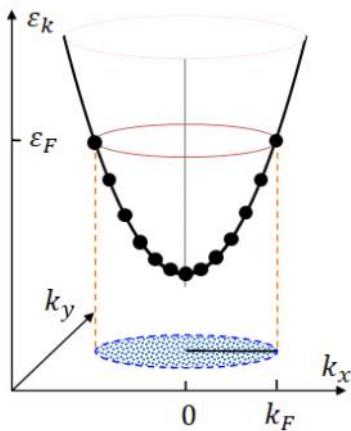
- Effects of the distribution function:



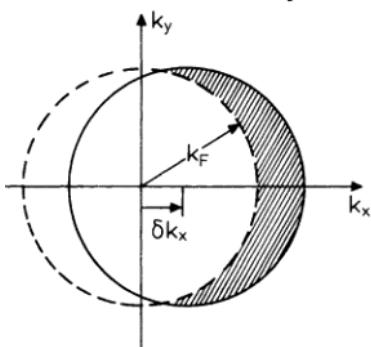
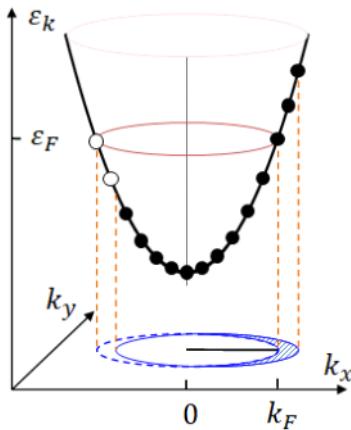
The new Fermi distribution  $f$  only differs significantly from the equilibrium distribution  $f_0$  in the vicinity of the Fermi energy.

- Effects of the Fermi surface:

Before the field applied



Apply the field

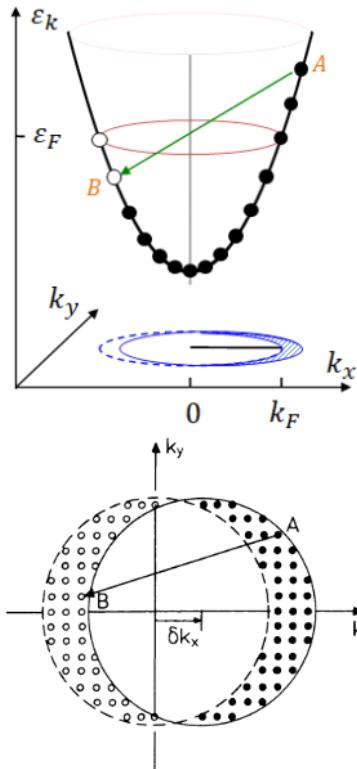


The great majority of the electrons cancel each other pairwise, electrons in the shaded area remain uncompensated and produce the observed current.

(3) Relaxation back to equilibrium

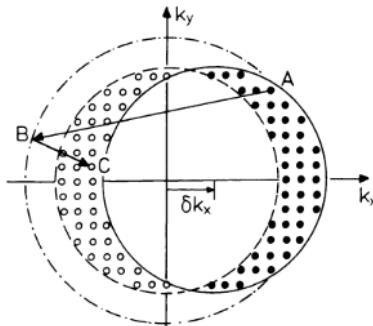
The stationary non-equilibrium distribution is represented as a displaced Fermi sphere.

1. Inelastic scattering



Since the states  $A$  and  $B$  are at different energy states, the relaxation back to equilibrium must involve inelastic scattering.

2. Elastic scattering



For purely elastic scattering, the Fermi sphere would simply

expand. The equilibrium can only be achieved by inelastic scattering into states  $\mathcal{C}$ .

# 6-3 Transport Coefficients

Tuesday, May 14, 2013 4:08 PM

## A. COEFFICIENTS OF TRANSPORT

- (1) An electron moving in an electric field and a magnetic field, the Boltzmann equation with the relaxation time approximation is

$$\vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar} \cdot \frac{\partial f}{\partial \vec{k}} + \frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}$$

Since  $\vec{F} = -e \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right)$

$$\vec{v} \cdot \frac{\partial f}{\partial \vec{r}} - \frac{e}{\hbar} \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \cdot \frac{\partial f}{\partial \vec{k}} + \frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}$$

- (2) Assume an applied external field is small and the non-equilibrium distribution function is a small deviation from the equilibrium distribution function,  $f = f_0 + \delta f$ .

$$\underbrace{\vec{v} \cdot \frac{\partial}{\partial \vec{r}} (f_0 + \delta f)}_{\textcircled{1}} - \underbrace{\frac{e}{\hbar} \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \cdot \frac{\partial}{\partial \vec{k}} (f_0 + \delta f)}_{\textcircled{2}} + \underbrace{\frac{\partial}{\partial t} (f_0 + \delta f)}_{\textcircled{3}} = -\frac{\delta f}{\tau}$$

The equation above is a non-linear equation. We would like to make a linearized equation.

Case ① (temperature effect):

$$\frac{\partial}{\partial \vec{r}} (f_0 + \delta f) = \left( \frac{\partial f_0}{\partial \mu} \nabla \mu + \frac{\partial f_0}{\partial T} \nabla T \right) + \left( \frac{\partial \delta f}{\partial \mu} \nabla \mu + \frac{\partial \delta f}{\partial T} \nabla T \right)$$

Since  $\frac{\partial \delta f}{\partial \mu}$  and  $\frac{\partial \delta f}{\partial T}$  of the second term are smaller compared to the first term, we ignore these terms and obtain

$$\begin{aligned} \frac{\partial}{\partial \vec{r}} (f_0 + \delta f) &\approx \frac{\partial f_0}{\partial \mu} \nabla \mu + \frac{\partial f_0}{\partial T} \nabla T \\ &= -\frac{\partial f_0}{\partial \varepsilon} \nabla \mu - \frac{\varepsilon - \mu}{T} \frac{\partial f_0}{\partial \varepsilon} \nabla T \\ &= \left[ \nabla \mu + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \end{aligned}$$

Case ② (electric & magnetic field):

$$-\frac{e}{\hbar} \vec{E} \cdot \frac{\partial}{\partial \vec{k}} (f_0 + \delta f) = -\frac{e}{\hbar} \vec{E} \cdot \frac{\partial f_0}{\partial \vec{k}} - \frac{e}{\hbar} \vec{E} \cdot \frac{\partial \delta f}{\partial \vec{k}}$$

Since  $\frac{\partial \delta f}{\partial \vec{k}}$  of the second term is smaller compared to the first term, we ignore the term and obtain

$$\begin{aligned} -\frac{e}{\hbar} \vec{E} \cdot \frac{\partial}{\partial \vec{k}} (f_0 + \delta f) &\approx -\frac{e}{\hbar} \vec{E} \cdot \frac{\partial f_0}{\partial \vec{k}} \\ &= -\frac{e}{\hbar} \vec{E} \cdot \frac{\partial f_0}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial \vec{k}} \\ &= -\frac{e}{\hbar} \vec{E} \cdot \hbar \vec{v} \frac{\partial f_0}{\partial \varepsilon} \\ &= \vec{v} \cdot e \vec{E} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \end{aligned}$$

$$\begin{aligned} -\frac{e}{\hbar c} \vec{v} \times \vec{B} \cdot \frac{\partial}{\partial \vec{k}} (f_0 + \delta f) &= -\frac{e}{\hbar c} \vec{v} \times \vec{B} \cdot \frac{\partial f_0}{\partial \vec{k}} - \frac{1}{c} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{k}} \\ &= \underbrace{-\frac{e}{c} \vec{v} \times \vec{B} \cdot \vec{v} \frac{\partial f_0}{\partial \varepsilon}}_{=0} - \frac{1}{c} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{k}} \\ &= -\frac{1}{c} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{k}} \end{aligned}$$

Case ③ (time-dependent):

$$\frac{\partial}{\partial t} (f_0 + \delta f) = \underbrace{\frac{\partial f_0}{\partial t}}_{=0} + \frac{\partial \delta f}{\partial t} = \frac{\partial \delta f}{\partial t}$$

The linearized Boltzmann equation is

$$\begin{aligned} &\underbrace{\vec{v} \cdot \left[ \nabla \mu + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) + \vec{v} \cdot e \vec{E} \left( -\frac{\partial f_0}{\partial \varepsilon} \right)}_{= -\frac{\delta f}{\tau}} - \frac{e}{\hbar c} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{k}} + \frac{\partial \delta f}{\partial t} \\ &\Rightarrow \vec{v} \cdot \left[ e \vec{E} + \nabla \mu + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) - \frac{e}{\hbar c} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{k}} + \frac{\partial \delta f}{\partial t} = -\frac{\delta f}{\tau} \end{aligned}$$

Since  $-e \vec{E} = \vec{F} = -\nabla \phi$

$$\text{Let } \vec{\mathcal{E}} = \nabla \left( \phi + \frac{\mu}{e} \right)$$

$\vec{\mathcal{E}}$  is the gradient of the electrochemical potential; we'll henceforth refer to  $\vec{\mathcal{E}}$  as the electric field.

We obtain the linearized Boltzmann equation,

$$\vec{v} \cdot \left[ e\vec{\mathcal{E}} + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) - \frac{e}{\hbar c} \vec{v} \times \vec{B} \cdot \frac{\partial \delta f}{\partial \vec{k}} + \frac{\partial \delta f}{\partial t} = -\frac{\delta f}{\tau}$$

(3) Consider the case where  $\vec{B} = 0$  and the steady state  $\frac{\partial \delta f}{\partial t} = 0$ :

$$\vec{v} \cdot \left[ e\vec{\mathcal{E}} + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) = -\frac{\delta f}{\tau}$$

$$\delta f = -\tau \vec{v} \cdot \left[ e\vec{\mathcal{E}} + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right)$$

The electric current density:

$$\begin{aligned} \vec{j}_e &= \int (-e) \vec{v} \delta f \frac{d^3 k}{(2\pi)^3} \\ &= e \int \vec{v} \tau \vec{v} \cdot \left[ e\vec{\mathcal{E}} + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \\ &= e \int \left\{ \vec{v} \tau \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \cdot [e\vec{\mathcal{E}}] + \vec{v} \tau \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \cdot \left[ (\varepsilon - \mu) \frac{\nabla T}{T} \right] \right\} \frac{d^3 k}{(2\pi)^3} \\ &= e^2 \int \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \cdot \vec{\mathcal{E}} - e \int (\varepsilon - \mu) \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \cdot \left[ -\frac{\nabla T}{T} \right] \end{aligned}$$

The thermal current density:

$$\begin{aligned} \vec{j}_Q &= \int (\varepsilon - \mu) e \vec{v} \delta f \frac{d^3 k}{(2\pi)^3} \\ &= -e \int (\varepsilon - \mu) \vec{v} \tau \vec{v} \cdot \left[ e\vec{\mathcal{E}} + (\varepsilon - \mu) \frac{\nabla T}{T} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \\ &= -e^2 \int (\varepsilon - \mu) \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \cdot \vec{\mathcal{E}} \\ &\quad + e \int (\varepsilon - \mu)^2 \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \cdot \left[ -\frac{\nabla T}{T} \right] \end{aligned}$$

Let

$$\Lambda^{(v)} = e^2 \int (\varepsilon - \mu)^v \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}$$

$$L_{11} = \Lambda^{(0)} = e^2 \int \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial E} \right) \frac{d^3 k}{(2\pi)^3}$$

$$L_{12} = L_{21} = -\frac{1}{e} \Lambda^{(1)} = -e \int (\varepsilon - \mu) \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}$$

$$L_{22} = \frac{1}{e^2} \Lambda^{(2)} = \int (\varepsilon - \mu)^2 \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}$$

$L_{11}$ ,  $L_{12}$ ,  $L_{21}$ , and  $L_{22}$  are called coefficients of transport.

The set of equations of the electric and thermal current density are

$$\vec{J}_e = L_{11} \cdot \vec{\mathcal{E}} + L_{12} \cdot \left[ -\frac{\nabla T}{T} \right]$$

$$\vec{J}_Q = L_{21} \cdot \vec{\mathcal{E}} + L_{22} \cdot \left[ -\frac{\nabla T}{T} \right]$$

In the matrix form

$$\begin{pmatrix} \vec{J}_e \\ \vec{J}_Q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \vec{\mathcal{E}} \\ -\frac{\nabla T}{T} \end{pmatrix}$$

(4) We can derive the measurable quantities from coefficients of transport.

1. DC electric conductivity

$$\vec{J}_e = L_{11} \vec{E} = \bar{\sigma} \vec{E}$$

2. Thermal conductivity is defined as the ratio of the thermal current  $\vec{J}_Q$  to  $-\nabla T$  under conditions of zero electric current.

$$\vec{J}_e = 0 \Rightarrow L_{11} \cdot \vec{\mathcal{E}} + L_{12} \cdot \left[ -\frac{\nabla T}{T} \right] = 0$$

$$\vec{J}_Q = L_{21} \cdot \vec{\mathcal{E}} + L_{22} \cdot \left[ -\frac{\nabla T}{T} \right]$$

$$= L_{21} \frac{L_{12}}{L_{11}} \cdot \frac{\nabla T}{T} - L_{22} \cdot \frac{\nabla T}{T}$$

$$= \frac{L_{22}L_{11} - L_{21}L_{12}}{L_{11}} \cdot \left( -\frac{\nabla T}{T} \right)$$

$$= \bar{\kappa} T \cdot \left( -\frac{\nabla T}{T} \right)$$

## B. CONDUCTIVITY OF METALS

(1) DC electric conductivity

$$\bar{\sigma} = L_{11} = \Lambda^{(0)} = e^2 \int \tau \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}$$

The diagonal electric conductivity:

$$\sigma = e^2 \int \tau \frac{v^2}{3} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} = \frac{2e^2 \tau}{3m} \int \varepsilon \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}$$

Use the density of states:

$$\sigma = \frac{2e^2\tau}{3m} \int \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \varepsilon g(\varepsilon) d\varepsilon$$

Use Sommerfeld expansion:

$$\sigma = \frac{2e^2\tau}{3m} \times \frac{3n}{2} \left\{ 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F^2} \right\} = \frac{ne^2\tau}{m} \left\{ 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F^2} \right\}$$

OS:

Method 1:

Directly use Sommerfeld expansion

$$\int_0^\infty \left( -\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) G(\varepsilon) d\varepsilon = G(\mu) + \frac{\pi^2}{6} (k_B T)^2 G''(\mu)$$

$$G(\varepsilon) = \varepsilon g(\varepsilon) = \varepsilon \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} = \frac{3n\varepsilon^{3/2}}{2\varepsilon_F^{3/2}}$$

$$G''(\varepsilon) = \frac{3n}{2} \frac{3}{4} \frac{\varepsilon^{-1/2}}{\varepsilon_F^{3/2}}$$

$$\begin{aligned} \int \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \varepsilon g(\varepsilon) d\varepsilon &= \frac{3n\varepsilon_F^{3/2}}{2\varepsilon_F^{3/2}} + \frac{\pi^2}{6} (k_B T)^2 \frac{3n}{2} \frac{3}{4} \frac{\varepsilon_F^{-1/2}}{\varepsilon_F^{3/2}} \\ &= \frac{3n}{2} \left( 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F^2} \right) \end{aligned}$$

Method 2:

Integration by parts

$$\int \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \varepsilon g(\varepsilon) d\varepsilon = \frac{3}{2} \int f_0 g(\varepsilon) d\varepsilon$$

Use Sommerfeld expansion

$$\begin{aligned} \int f_0 g(\varepsilon) d\varepsilon &= \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \\ &= n + \frac{\pi^2}{6} (k_B T)^2 \frac{3n}{4} \frac{1}{\varepsilon_F^2} \\ &= n \left( 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F^2} \right) \end{aligned}$$

(2) AC electric conductivity

$$\vec{E} = \vec{E}_0 e^{-i\omega t} = E_0 e^{-i\omega t} \hat{x}$$

$$\frac{\partial \delta f}{\partial t} + \vec{v} e \vec{E}_0 e^{-i\omega t} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) = -\frac{\delta f}{\tau}$$

$$\delta f = \frac{e \vec{E}_0 \cdot \vec{v} \tau}{1 - i\omega \tau} \frac{\partial f_0}{\partial \varepsilon} e^{-i\omega t} = \frac{-e\tau}{1 - i\omega \tau} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \vec{E}$$

$$\vec{J}_e = \int (-e) \vec{v} \delta f \frac{d^3 k}{(2\pi)^3} = \underbrace{\frac{e^2 \tau}{1 - i\omega \tau} \int \vec{v} \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}}_{\sigma(\omega)} \vec{E}$$

$$\sigma(\omega) = \frac{1}{1 - i\omega \tau} \Lambda^{(0)} = \frac{1}{1 - i\omega \tau} \frac{n e^2 \tau}{m} \left\{ 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F^2} \right\}$$

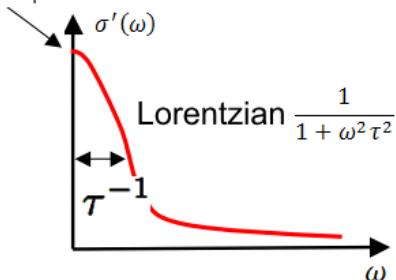
1. At zero temperature ( $T = 0$ )

$$\sigma(\omega) = \frac{n e^2 \tau}{m} \frac{1}{1 - i\omega \tau} = \sigma'(\omega) + \sigma''(\omega)$$

The dissipative part of the conductivity is  $\text{Re } \sigma(\omega) = \sigma'(\omega)$

$$\sigma'(\omega) = \frac{n e^2 \tau}{m} \frac{1}{1 + \omega^2 \tau^2}$$

Drude peak



The peak at  $\omega = 0$  is known as the Drude peak  
OS:

$$k_B T \ll E_F \Rightarrow -\frac{\partial f_0}{\partial \varepsilon} \approx \delta(\varepsilon_F - \varepsilon)$$

$$I = \int v_i v_j \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}$$

$$= \frac{1}{4\pi^3} \int v_i v_j \delta(\varepsilon_F - \varepsilon) dS_E \frac{d\varepsilon}{|\nabla_k \varepsilon|}$$

$$= \frac{1}{4\pi^3} \int_{E=\varepsilon_F} v_i v_j \frac{dS_E}{\hbar |\vec{v}|}$$

Only electrons in the vicinity of the Fermi energy are relevant for current transport in a metal.

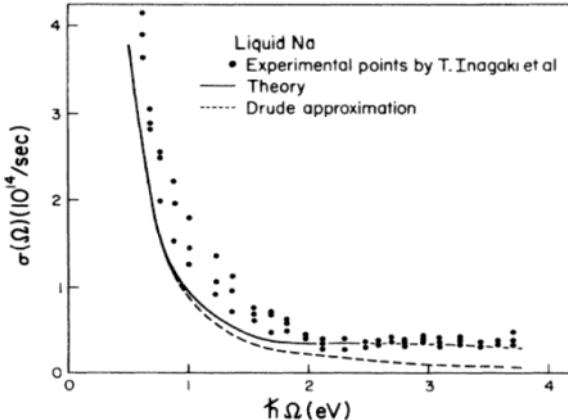
$$I = \frac{1}{4\pi^3} \frac{\nu(\varepsilon_F)}{3\hbar} \int_{E=\varepsilon_F} dS_E = \frac{1}{4\pi^3} \frac{k_F}{3m} 4\pi k_F^2 = \frac{k_F^3}{3\pi^2 m}$$

Since  $k_F^3 = 3\pi^2 n$  [c.f.5-2]

$$I = \frac{1}{3\pi^2 m} 3\pi^2 n = \frac{n}{m}$$

2. At low temperature

$$\sigma(\omega) = \frac{ne^2\tau}{m} \frac{1}{1 - i\omega\tau} \left\{ 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F^2} \right\}$$



(3) The thermal conductivity:

$$\bar{\kappa}T = \frac{L_{22}L_{11} - L_{21}L_{12}}{L_{11}}$$

The diagonal electric conductivity:

$$\Lambda^{(\nu)} = e^2 \int (\varepsilon - \mu)^\nu \tau \vec{v} \cdot \vec{v} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3} \approx \frac{2e^2\tau}{3m} \int \varepsilon^{\nu+1} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) g(\varepsilon) d\varepsilon$$

OS:

Directly use Sommerfeld expansion

$$\int_0^\infty \left( -\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) G(\varepsilon) d\varepsilon = G(\mu) + \frac{\pi^2}{6} (k_B T)^2 G''(\mu)$$

$$G(\varepsilon) = \varepsilon^{\nu+1} g(\varepsilon) = \frac{3n\varepsilon^{\nu+3/2}}{2\varepsilon_F^{3/2}}$$

$$G''(\varepsilon) = \frac{3n}{2} \left( \nu + \frac{3}{2} \right) \left( \nu + \frac{1}{2} \right) \frac{\varepsilon_F^{\nu-1/2}}{\varepsilon_F^{3/2}}$$

$$\int_0^\infty \left( -\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) G(\varepsilon) d\varepsilon = \frac{3n}{2} \varepsilon_F^\nu + \frac{\pi^2}{6} (k_B T)^2 \frac{3n}{2} \left( \nu + \frac{3}{2} \right) \left( \nu + \frac{1}{2} \right) \varepsilon_F^{\nu-2}$$

$$= \frac{3n}{2} \left\{ \varepsilon_F^\nu + \frac{\pi^2}{6} (k_B T)^2 \left( \nu + \frac{3}{2} \right) \left( \nu + \frac{1}{2} \right) \varepsilon_F^{\nu-2} \right\}$$

$$\Lambda^{(\nu)} = \frac{ne^2\tau}{m} \left\{ \varepsilon_F^\nu + \frac{\pi^2}{6} (k_B T)^2 \left( \nu + \frac{3}{2} \right) \left( \nu + \frac{1}{2} \right) E_F^{\nu-2} \right\}$$

$$L_{11} = \Lambda^{(0)} = \frac{ne^2\tau}{m} \left\{ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\varepsilon_F} \right)^2 \right\}$$

$$L_{21} = -\frac{1}{e} \Lambda^{(1)} = -\frac{net\tau}{m} \left\{ \varepsilon_F + \frac{5\pi^2}{8} \frac{(k_B T)^2}{\varepsilon_F} \right\}$$

$$L_{22} = \frac{1}{e^2} \Lambda^{(2)} = \frac{n\tau}{m} \left\{ \varepsilon_F^2 + \frac{35\pi^2}{24} (k_B T)^2 \right\}$$

$$\kappa T = \frac{L_{22}L_{11} - L_{21}L_{12}}{L_{11}} = \frac{n\tau}{m} \varepsilon_F^2 \left\{ \frac{\left( \frac{38\pi^2}{24} - \frac{10\pi^2}{8} \right) \left( \frac{k_B T}{\varepsilon_F} \right)^2}{1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\varepsilon_F} \right)^2} \right\} \approx \frac{\pi^2 n\tau}{3 m} k_B^2 T^2$$

$$\kappa = \frac{\pi^2 n\tau}{3 m} k_B^2 T$$

(4) Wiedermann-Franz law

$$\frac{\kappa}{\sigma_0} = \frac{\frac{\pi^2 n\tau}{3 m} k_B^2 T}{\frac{ne^2\tau}{m}} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 T$$

$$L = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.45 \times 10^{-8} \text{ W}\Omega/\text{K}^2$$

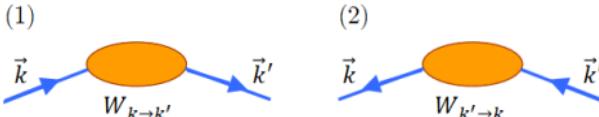
# 6-4 Impurity Scattering

Tuesday, May 14, 2013 4:08 PM

## A. ELASTIC SCATTERING

- (1) Collision integral

Processes:



$$(1) = W_{k \rightarrow k'} \times [1 - f(\vec{k})] f(\vec{k}')$$

$$(2) = W_{k' \rightarrow k} \times f(\vec{k}) [1 - f(\vec{k}')]$$

where  $W$  is the scattering rate. The scattering from a static potential (impurity) induces transitions between  $\vec{k}$  and  $\vec{k}'$ .

The collision integral may be expressed as

$$\mathcal{I}_{\text{coll}} = \sum_{k'} [W_{k \rightarrow k'} [1 - f(\vec{k})] f(\vec{k}') - W_{k' \rightarrow k} f(\vec{k}) [1 - f(\vec{k}')]]$$

For a system with time inversion symmetry, we have  $W_{k \rightarrow k'} = W_{k' \rightarrow k} \equiv W(\vec{k}, \vec{k}')$ ,

$$\begin{aligned} \mathcal{I}_{\text{coll}} &= \sum_{k'} W(\vec{k}, \vec{k}') [[1 - f(\vec{k})] f(\vec{k}') - f(\vec{k}) [1 - f(\vec{k}')]] \\ &= \sum_{k'} W(\vec{k}, \vec{k}') [f(\vec{k}') - f(\vec{k}) f(\vec{k}') - f(\vec{k}) + f(\vec{k}) f(\vec{k}')] \\ &= \sum_{k'} W(\vec{k}, \vec{k}') [f(\vec{k}') - f(\vec{k})] \end{aligned}$$

Usually, we study processes close to equilibrium and assume a small deviation from the thermal equilibrium, i.e.,  $f = f_0 + \delta f$ .

$$\mathcal{I}_{\text{coll}} = \sum_{k'} W(\vec{k}, \vec{k}') [f_0(\vec{k}') + \delta f(\vec{k}') - f_0(\vec{k}) - \delta f(\vec{k})]$$

For the elastic scattering,  $|\vec{k}| = |\vec{k}'| \Rightarrow \varepsilon_k = \varepsilon_{k'} \Rightarrow f_0(\vec{k}') = f_0(\vec{k})$

$$\mathcal{I}_{\text{coll}} = \sum_{k'} W(\vec{k}, \vec{k}') [\delta f(\vec{k}') - \delta f(\vec{k})]$$

(2) The transition rate can be obtained by Fermi golden rule

$$W(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar} \left| \langle \vec{k}' | \hat{V}(\vec{r}) | \vec{k} \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_{k'})$$

where  $\hat{V}(\vec{r})$  is the sum over individual impurity potential

$$\hat{V}(\vec{r}) = \sum_i v_{\text{imp}}(\vec{r} - \vec{R}_i)$$

$$\begin{aligned} \langle \vec{k}' | \hat{V}(\vec{r}) | \vec{k} \rangle &= \sum_i \int v_{\text{imp}}(\vec{r} - \vec{R}_i) \frac{1}{\sqrt{\mathcal{V}}} e^{-i\vec{k}' \cdot \vec{r}} \frac{1}{\sqrt{\mathcal{V}}} e^{i\vec{k} \cdot \vec{r}} d^3 r \\ &= \frac{1}{\mathcal{V}} \sum_i \int v_{\text{imp}}(\vec{r} - \vec{R}_i) e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}} d^3 r \end{aligned}$$

Let  $\vec{r} - \vec{R}_i = \vec{r}'$

$$\langle \vec{k}' | \hat{V}(\vec{r}) | \vec{k} \rangle = \frac{1}{\mathcal{V}} \sum_{iG} e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_i} \int v_{\text{imp}}(\vec{r}') e^{-i(\vec{k} - \vec{k}') \cdot \vec{r}'} d^3 r'$$

$$= \frac{1}{\mathcal{V}} \sum_i e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_i} v_{\text{imp}}(\vec{k} - \vec{k}')$$

$$\begin{aligned} W(\vec{k}, \vec{k}') &= \frac{2\pi}{\hbar} \left| \frac{1}{\mathcal{V}} \sum_j e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_j} v_{\text{imp}}(\vec{k} - \vec{k}') \right. \\ &\quad \times \left. \frac{1}{\mathcal{V}} \sum_i e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_i} v_{\text{imp}}(\vec{k} - \vec{k}') \right| \delta(\varepsilon_k - \varepsilon_{k'}) \\ &= \frac{2\pi}{\hbar} \frac{1}{\mathcal{V}^2} \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \delta(\varepsilon_k - \varepsilon_{k'}) \sum_{ij} e^{i(\vec{k} - \vec{k}') \cdot (\vec{R}_j - \vec{R}_i)} \end{aligned}$$

Because the positions of the impurities are random, the distance between them is much greater than interatomic spacing  $a$ . So we can average over their positions,

$$\overline{\sum_{i,j} e^{i(\vec{k} - \vec{k}') \cdot (\vec{R}_j - \vec{R}_i)}} = N_{\text{imp}} + N_{\text{imp}}(N_{\text{imp}} - 1) \delta_{k,k'}$$

where the first term is the one with  $i = j$ , and the second term is the ones with  $\vec{k} = \vec{k}', i \neq j$ .

$$W(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar} \frac{1}{\mathcal{V}^2} \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \delta(\varepsilon_k - \varepsilon_{k'}) [N_{\text{imp}} + N_{\text{imp}}(N_{\text{imp}} - 1) \delta_{k,k'}]$$

$$\begin{aligned}
\mathcal{J}_{\text{coll}} &= \frac{2\pi}{\hbar} \frac{1}{\mathcal{V}^2} \sum_{k'} \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \delta(\varepsilon_k - \varepsilon_{k'}) \left[ N_{\text{imp}} + N_{\text{imp}}(N_{\text{imp}} - 1) \delta_{k,k'} \right] \\
&\quad \times \left[ \delta f(\vec{k}') - \delta f(\vec{k}) \right] \\
&= \frac{2\pi N_{\text{imp}}}{\hbar} \frac{1}{\mathcal{V}^2} \sum_{k'} \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \delta(\varepsilon_k - \varepsilon_{k'}) \left[ \delta f(\vec{k}') - \delta f(\vec{k}) \right] \\
&\quad + \frac{2\pi N_{\text{imp}}(N_{\text{imp}} - 1)}{\hbar} \frac{1}{\mathcal{V}^2} \left| v_{\text{imp}}(0) \right|^2 \delta(0) \left[ \delta f(\vec{k}) - \delta f(\vec{k}) \right] \\
&= \frac{2\pi N_{\text{imp}}}{\hbar} \frac{1}{\mathcal{V}^2} \sum_{k'} \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \delta(\varepsilon_k - \varepsilon_{k'}) \left[ \delta f(\vec{k}') - \delta f(\vec{k}) \right]
\end{aligned}$$

Since

$$\begin{aligned}
n_{\text{imp}} &= \frac{N_{\text{imp}}}{\mathcal{V}} \quad \text{and} \quad \sum_{k'} = \mathcal{V} \int \frac{d^3 k'}{(2\pi)^3} \\
\delta(\varepsilon_k - \varepsilon_{k'}) &= \delta\left(\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k'^2}{2m}\right) = \frac{\delta(k - k')}{\hbar^2 k/m} \\
\mathcal{J}_{\text{coll}} &= \frac{2\pi n_{\text{imp}}}{\hbar} \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{\hbar^2 k/m} \left[ \delta f(\vec{k}') - \delta f(\vec{k}) \right] \frac{d^3 k'}{(2\pi)^3} \\
&= \frac{mn_{\text{imp}}}{4\pi^2 \hbar^3} \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{k} \left[ \delta f(\vec{k}') - \delta f(\vec{k}) \right] d^3 k'
\end{aligned}$$

## B. RELAXATION TIME

- (1) Consider the simplest case of a system at constant temperature subject to a small uniform electric field  $\vec{E}$ . The Boltzmann equation is

$$\mathcal{J}_{\text{coll}} = -e\vec{E} \cdot \frac{\partial f}{\partial \vec{k}} = -e\vec{E} \cdot \vec{v}_k \frac{\partial f_0}{\partial \varepsilon}$$

In the relaxation-time approximation,

$$\begin{aligned}
\mathcal{J}_{\text{coll}} &= -\frac{f - f_0}{\tau} = -\frac{\delta f}{\tau} \\
\Rightarrow \delta f &= \tau e\vec{E} \cdot \vec{v}_k \frac{\partial f_0}{\partial \varepsilon}
\end{aligned}$$

Thus, we obtain

$$\begin{aligned}
-e\vec{E} \cdot \vec{v}_k \frac{\partial f_0}{\partial \varepsilon} &= \frac{mn_{\text{imp}}}{4\pi^2 \hbar^3} \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{k} \\
&\quad \times \left[ \tau(\varepsilon_{k'}) e\vec{E} \cdot \vec{v}_{k'} \frac{\partial f_0}{\partial \varepsilon} - \tau(\varepsilon_k) e\vec{E} \cdot \vec{v}_k \frac{\partial f_0}{\partial \varepsilon} \right] d^3 k'
\end{aligned}$$

Due to the isotropic of the system, we must have  $\tau(\varepsilon_k)$  is a function only of the magnitude of  $k$ .

$$\vec{v}_k = \frac{mn_{\text{imp}}}{4\pi^2\hbar^3} \tau(\varepsilon_k) \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{k} [\vec{v}_k - \vec{v}_{k'}] d^3 k'$$

Since  $\vec{v}_k = \hbar \vec{k} / m$

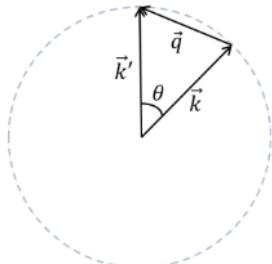
$$\frac{\hbar \vec{k}}{m} = \frac{n_{\text{imp}}}{4\pi^2\hbar^2} \tau(\varepsilon_k) \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{k} [\vec{k} - \vec{k}'] d^3 k'$$

Since the scattering is elastic,  $|\vec{k}| = |\vec{k}'|$

$$\frac{\hbar \hat{k}}{m} = \frac{n_{\text{imp}}}{4\pi^2\hbar^2} \tau(\varepsilon_k) \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{k} [\hat{k} - \hat{k}'] d^3 k'$$

Dot product  $\hat{k}$  on both sides, we obtain

$$\frac{\hbar}{m} = \frac{n_{\text{imp}}}{4\pi^2\hbar^2} \tau(\varepsilon_k) \int \left| v_{\text{imp}}(\vec{k} - \vec{k}') \right|^2 \frac{\delta(k - k')}{k} [1 - \hat{k} \cdot \hat{k}'] d^3 k'$$



$$1 - \hat{k} \cdot \hat{k}' = 1 - \cos \theta$$

$$\begin{aligned} \frac{1}{\tau(\varepsilon_k)} &= \frac{mn_{\text{imp}}}{4\pi^2\hbar^3} \int \left| v_{\text{imp}}(\vec{q}) \right|^2 \frac{\delta(k - k')}{k} (1 - \cos \theta) k'^2 dk' \sin \theta d\theta d\phi \\ &= \frac{mn_{\text{imp}}}{2\pi\hbar^3} \int \left| v_{\text{imp}}(\vec{q}) \right|^2 \frac{\delta(k - k')}{k} (1 - \cos \theta) k'^2 dk' \sin \theta d\theta \\ &= \frac{mn_{\text{imp}}}{2\pi\hbar^3} k \int \left| v_{\text{imp}}(\vec{q}) \right|^2 (1 - \cos \theta) \sin \theta d\theta \end{aligned}$$

- (2) Use the differential scattering cross section under the Born approximation,

$$\sigma(\theta) = \left( \frac{m}{2\pi\hbar^2} \right)^2 \left| v_{\text{imp}}(\vec{q}) \right|^2$$

$$\begin{aligned} \frac{1}{\tau(\varepsilon_k)} &= \frac{2\pi\hbar k n_{\text{imp}}}{m} \int \sigma(\theta) (1 - \cos \theta) \sin \theta d\theta \\ &= 2\pi v_k n_{\text{imp}} \int \sigma(\theta) (1 - \cos \theta) \sin \theta d\theta \end{aligned}$$

The factor  $(1 - \cos \theta)$  indicates that forward scattering ( $\theta = 0$ ) does not contribute to the scattering rate, i.e., the forward scattering does not degrade the current.

Assume that electrons involved only at the Fermi energy, i.e.,  $k \rightarrow k_F$

$$\frac{1}{\tau(\varepsilon_F)} = 2\pi\nu_F n_{\text{imp}} \int \sigma_F(\theta)(1 - \cos \theta) \sin \theta d\theta$$

- (3) The differential scattering cross section due to the Coulomb potential

$$U(r) = -\frac{Ze^2}{r} \text{ and } U(q) = -\frac{4\pi Ze^2}{q^2}$$

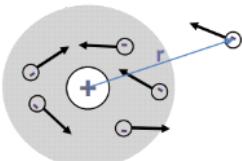
OS:

$$\int \frac{e^{-i\vec{q} \cdot \vec{r}}}{r} d^3r = \lim_{a \rightarrow 0} \int \frac{e^{-i\vec{q} \cdot \vec{r}}}{r} e^{-ar} d^3r = \lim_{a \rightarrow 0} \frac{4\pi}{q^2 + a^2} = \frac{4\pi}{q^2}$$

$$\Rightarrow \sigma(\theta) = \left( \frac{Ze^2}{4E \sin^2 \frac{\theta}{2}} \right)^2$$

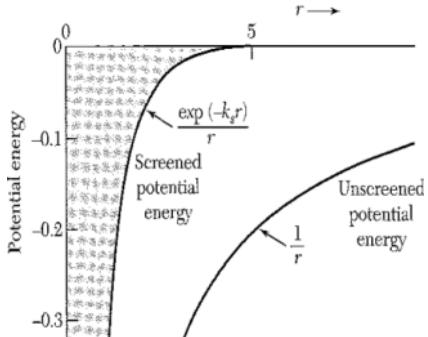
As  $\theta \rightarrow 0$ ,  $\sigma(\theta)$  diverges logarithmically.

In the one electron picture, the actual potential seen by electrons is screened by the other electrons in the system.



The screening potential is

$$U(r) = -\frac{Ze}{r} e^{-r/\lambda} \text{ and } U(q) = -\frac{4\pi Ze^2}{q^2 + \lambda^{-2}}, \quad \lambda = \left( \frac{4\pi e^2}{\epsilon} g(\varepsilon_F) \right)^{-1/2}$$



$$\Rightarrow \sigma(\theta) = \left( \frac{Ze^2}{4E \left( \sin^2 \frac{\theta}{2} + (2k_F\lambda)^{-2} \right)} \right)^2$$

$$\frac{1}{\tau(\varepsilon_F)} = 2\pi n_{\text{imp}} v_F \left( \frac{Ze^2}{4\varepsilon} \right)^2 \int_0^\pi \left( \frac{1}{\sin^2 \frac{\theta}{2} + (2k_F\lambda)^{-2}} \right)^2 (1 - \cos \theta) \sin \theta d\theta$$

$$= 2\pi n_{\text{imp}} v_F \left( \frac{Ze^2}{2\varepsilon} \right)^2 \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}$$

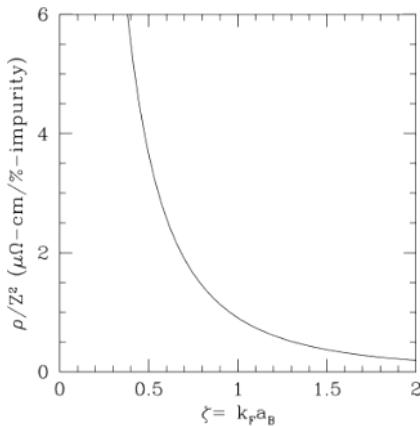
where  $\zeta = \frac{4}{\pi} k_F^2 \lambda^2 = \frac{\hbar^2 k_F}{me^2} = k_F a_0$   
and  $a_0$  is the effective Bohr radius

(4) The resistivity

$$\rho = \frac{m}{ne^2 \tau(\varepsilon_F)} = \frac{h}{e^2} a_0 Z^2 \frac{n_{\text{imp}}}{n} \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}$$

For  $h/e^2 = 25,813 \Omega$  and  $a_0 \approx 0.529 \text{ \AA}$

$$\rho = 1.37 \times 10^{-4} \Omega \cdot \text{cm} \times Z^2 \frac{n_{\text{imp}}}{n} \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}$$



# 6-5 Phonon Scattering

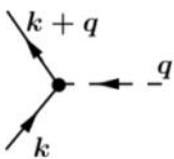
Tuesday, December 20, 2011 8:30 PM

## A. INELASTIC SCATTERING

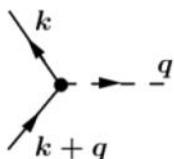
### (1) Collision integral

Processes:

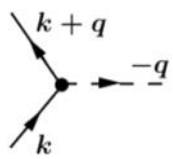
(1) Absorb  $q$



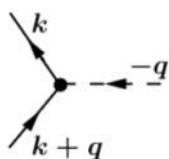
(2) Emit  $q$



(3) Emit  $-q$



(4) Absorb  $-q$



$$(1) = W_{(k,q) \rightarrow k+q} \times f_k(1 - f_{k+q}) \times n_q$$

$$(2) = W_{k+q \rightarrow (k,q)} \times f_{k+q}(1 - f_k) \times (n_q + 1)$$

$$(3) = W_{k \rightarrow (k+q,-q)} \times f_k(1 - f_{k+q}) \times (n_{-q} + 1)$$

$$(4) = W_{(k+q,-q) \rightarrow k} \times f_{k+q}(1 - f_k) \times n_{-q}$$

The collision integral may be expressed as

$$\begin{aligned} \mathcal{I}_{\text{coll}} = \sum_q & \left\{ W_{(k,q) \rightarrow k+q} f_k(1 - f_{k+q}) n_q \right. \\ & - W_{k+q \rightarrow (k,q)} f_{k+q}(1 - f_k)(n_q + 1) \\ & + W_{k \rightarrow (k+q,-q)} f_k(1 - f_{k+q})(n_{-q} + 1) \\ & \left. - W_{(k+q,-q) \rightarrow k} f_{k+q}(1 - f_k) n_{-q} \right\} \end{aligned}$$

For a system with time inversion symmetry, we have

$$W_{(k,q) \rightarrow k+q} = W_{k+q \rightarrow (k,q)} \equiv W(\vec{k}, \vec{q}; \vec{k} + \vec{q}), \text{ and}$$

$$W_{k \rightarrow (k+q,-q)} = W_{(k+q,-q) \rightarrow k} = W(\vec{k}; \vec{k} + \vec{q}, -\vec{q})$$

$$\begin{aligned} \mathcal{I}_{\text{coll}} = \sum_q & \left\{ W(\vec{k}, \vec{q}; \vec{k} + \vec{q}) [f_k(1 - f_{k+q}) n_q - f_{k+q}(1 - f_k)(n_q + 1)] \right. \\ & \left. + W(\vec{k}; \vec{k} + \vec{q}, -\vec{q}) [f_k(1 - f_{k+q})(n_{-q} + 1) - f_{k+q}(1 - f_k)n_{-q}] \right\} \end{aligned}$$

Bloch ansatz: The phonon distribution remains in equilibrium even though the phonons scatter electrons and vice versa, i.e.,

$$n_q = n_q^0 \text{ (Bose distribution)}$$

$$\begin{aligned} \mathcal{I}_{\text{coll}} = & \sum_q \left\{ W(\vec{k}, \vec{q}; \vec{k} + \vec{q}) [f_k(1 - f_{k+q})n_q^0 - f_{k+q}(1 - f_k)(n_q^0 + 1)] \right. \\ & \left. + W(\vec{k}; \vec{k} + \vec{q}, -\vec{q}) [f_k(1 - f_{k+q})(n_{-q}^0 + 1) - f_{k+q}(1 - f_k)n_{-q}^0] \right\} \end{aligned}$$

Change dummy variable

$$-q \rightarrow q$$

$$\begin{aligned} \mathcal{I}_{\text{coll}} = & \sum_q \left\{ W(\vec{k}, \vec{q}; \vec{k} + \vec{q}) [f_k(1 - f_{k+q})n_q^0 - f_{k+q}(1 - f_k)(n_q^0 + 1)] \right. \\ & \left. + W(\vec{k}; \vec{k} - \vec{q}, \vec{q}) [f_k(1 - f_{k-q})(n_q^0 + 1) - f_{k-q}(1 - f_k)n_q^0] \right\} \end{aligned}$$

Usually, we study processes close to equilibrium and assume a small deviation from the thermal equilibrium, i.e.,  $f = f^0 + \delta f$ .

For  $W(\vec{k}, \vec{q}; \vec{k} + \vec{q})$  term:

$$\begin{aligned} & f_k(1 - f_{k+q})n_q^0 - f_{k+q}(1 - f_k)(n_q^0 + 1) \\ &= (f_k^0 + \delta f_k)(1 - f_{k+q}^0 - \delta f_{k+q})n_q^0 \\ & \quad - (f_{k+q}^0 + \delta f_{k+q})(1 - f_k^0 - \delta f_k)(n_q^0 + 1) \\ & \approx n_q^0 \delta f_k - n_q^0 \delta f_{k+q} - \delta f_{k+q} - f_k^0 \delta f_{k+q} + f_{k+q}^0 \delta f_k \\ &= (-n_q^0 - 1 + f_k^0) \delta f_{k+q} + (n_q^0 + f_{k+q}^0) \delta f_k \end{aligned}$$

For  $W(\vec{k}; \vec{k} - \vec{q}, \vec{q})$  term:

$$\begin{aligned} & f_k(1 - f_{k-q})(n_q^0 + 1) - f_{k-q}(1 - f_k)n_q^0 \\ &= (f_k^0 + \delta f_k)(1 - f_{k-q}^0 - \delta f_{k-q})(n_q^0 + 1) \\ & \quad - (f_{k-q}^0 + \delta f_{k-q})(1 - f_k^0 - \delta f_k)n_q^0 \\ & \approx n_q^0 \delta f_k + \delta f_k - f_{k-q}^0 \delta f_k - f_k^0 \delta f_{k-q} - n_q^0 \delta f_{k-q} \\ &= (n_q^0 + 1 - f_{k-q}^0) \delta f_k - (n_q^0 + f_k^0) \delta f_{k-q} \end{aligned}$$

$$\begin{aligned} \mathcal{I}_{\text{coll}} = & \sum_q \left\{ W(\vec{k}, \vec{q}; \vec{k} + \vec{q}) [(-n_q^0 - 1 + f_k^0) \delta f_{k+q} + (n_q^0 + f_{k+q}^0) \delta f_k] \right. \\ & \left. + W(\vec{k}; \vec{k} - \vec{q}, \vec{q}) [(n_q^0 + 1 - f_{k-q}^0) \delta f_k - (n_q^0 + f_k^0) \delta f_{k-q}] \right\} \end{aligned}$$

(2) The transition rate can be obtained by Fermi golden rule

$$W(\vec{k}, \vec{q}; \vec{k} + \vec{q}) = \frac{2\pi}{\hbar} \left| \langle k + q | \hat{V}_q | k \rangle \right|^2 \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q)$$

$$W(\vec{k}; \vec{k} - \vec{q}, \vec{q}) = \frac{2\pi}{\hbar} \left| \langle k - q | \hat{V}_q | k \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q)$$

where

$$\hat{V}_q = i|\vec{q}| \sqrt{\frac{2\hbar}{\rho_0 \omega_0 \mathcal{V}}} (V_0 \hat{c}_{k+q}^\dagger \hat{c}_k)$$

$$\langle k+q | V_0 \hat{c}_{k+q}^\dagger \hat{c}_k | k \rangle = \langle k-q | V_0 \hat{c}_{k-q}^\dagger \hat{c}_k | k \rangle = V_0$$

$$\text{Let } M_q = |\vec{q}| \sqrt{\frac{2\hbar}{\rho_0 \omega_0 \mathcal{V}}} V_0$$

$$W(\vec{k}, \vec{q}; \vec{k} + \vec{q}) = -\frac{2\pi}{\hbar} |M_q|^2 \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q)$$

$$W(\vec{k}; \vec{k} - \vec{q}, \vec{q}) = -\frac{2\pi}{\hbar} |M_q|^2 \delta(\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q)$$

Suppose the lattice vibration has Debye frequency, i.e.,  $\omega_q = sq$

$$\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q = \frac{\hbar^2 (\vec{k} + \vec{q})^2}{2m} - \frac{\hbar^2 k^2}{2m} - \hbar sq = \frac{\hbar^2 q^2}{2m} + \hbar v_k q \cos \theta - \hbar sq$$

$$\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 (\vec{k} - \vec{q})^2}{2m} - \hbar sq = -\frac{\hbar^2 q^2}{2m} + \hbar v_k q \cos \theta - \hbar sq$$

In the static potential limit (Born-Oppenheimer approximation)  $q^2 \ll 1$

$$\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q \approx \hbar v_k q \cos \theta - \hbar sq$$

$$\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q \approx \hbar v_k q \cos \theta - \hbar sq$$

$$\Rightarrow \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q) = \delta(\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q) = \delta(\hbar v_k q \cos \theta - \hbar sq)$$

$$\mathcal{J}_{\text{coll}} = -\frac{2\pi}{\hbar} \sum_q |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar sq) [(-n_q^0 - 1 + f_k^0) \delta f_{k+q}$$

$$+ (n_q^0 + f_{k+q}^0) \delta f_k + (n_q^0 + 1 - f_{k-q}^0) \delta f_k - (n_q^0 + f_k^0) \delta f_{k-q}]$$

$$= -\frac{2\pi}{\hbar} \sum_q |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar sq) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0)$$

$$\times (\delta f_k - \delta f_{k+q})$$

$$\text{Let } \sum_q = \mathcal{V} \int \frac{d^3 q}{(2\pi)^3}$$

$$\mathcal{J}_{\text{coll}} = -\frac{2\pi}{\hbar} \mathcal{V} \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar\omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0)$$

$$\times (\delta f_k - \delta f_{k+q}) \frac{d^3 q}{(2\pi)^3}$$

## B. BLOCH-GRÜNEISEN [grin'eisen] FORMULA

- (1) Consider the simplest case of a system at constant temperature subject to a small uniform electric field  $\vec{E}$ . The Boltzmann equation is

$$J_{\text{coll}} = -e\vec{E} \cdot \frac{\partial f}{\partial \vec{k}} = -e\vec{E} \cdot \vec{v}_k \frac{\partial f_0}{\partial \varepsilon}$$

In the relaxation-time approximation,

$$J_{\text{coll}} = -\frac{f - f_0}{\tau} = -\frac{\delta f}{\tau}$$

$$\Rightarrow \delta f = \tau e\vec{E} \cdot \vec{v}_k \frac{\partial f_0}{\partial \varepsilon}$$

Thus, we obtain

$$\begin{aligned} -e\vec{E} \cdot \vec{v}_k \frac{\partial f_k^0}{\partial \varepsilon} &= -\frac{\mathcal{V}}{4\pi^2\hbar} \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar \omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \\ &\quad \times \left[ \tau(\varepsilon_k) e\vec{E} \cdot \vec{v}_k \frac{\partial f_k^0}{\partial \varepsilon} - \tau(\varepsilon_{k+q}) e\vec{E} \cdot \vec{v}_{k+q} \frac{\partial f_{k+q}^0}{\partial \varepsilon} \right] d^3 q \end{aligned}$$

Due to the isotropic of the system, we must have  $\tau(\varepsilon_k)$  is a function only of the magnitude of  $k$  and  $f_k^0 = f_{k+q}^0$ .

$$\begin{aligned} \vec{v}_k &= \frac{\mathcal{V}}{4\pi^2\hbar} \tau(\varepsilon_k) \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar \omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \\ &\quad \times [\vec{v}_k - \vec{v}_{k+q}] d^3 q \end{aligned}$$

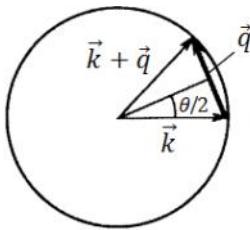
Since  $|\vec{v}_k| = |\vec{v}_{k+q}|$

$$\begin{aligned} \hat{v}_k &= \frac{\mathcal{V}}{4\pi^2\hbar} \tau(\varepsilon_k) \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar \omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \\ &\quad \times [\hat{v}_k - \hat{v}_{k+q}] d^3 q \end{aligned}$$

Dot product  $\hat{v}_k$  on both sides, we obtain

$$\begin{aligned} \frac{1}{\tau(\varepsilon_k)} &= \frac{\mathcal{V}}{4\pi^2\hbar} \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar \omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \\ &\quad \times [1 - \hat{v}_k \cdot \hat{v}_{k+q}] d^3 q \\ &= \frac{\mathcal{V}}{4\pi^2\hbar} \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar \omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \\ &\quad \times (1 - \cos \theta) q^2 dq \sin \theta d\theta d\phi \end{aligned}$$

- (2) Suppose that the scattering is of the small-angle type and electrons involved only at the Fermi energy,



$$\sin \frac{\theta}{2} = \frac{q}{2k_F} \xrightarrow{q \ll k_F} \theta = \frac{q}{k_F}$$

$$1 - \cos \theta \approx 1 - \left(1 - \frac{\theta^2}{2}\right) = \frac{\theta^2}{2} = \frac{q^2}{2k_F^2}$$

$$\begin{aligned} \frac{1}{\tau(\varepsilon_k)} &\approx \frac{\mathcal{V}}{4\pi^2\hbar} \int |M_q|^2 \delta(\hbar v_k q \cos \theta - \hbar \omega_q) (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \\ &\quad \times \frac{q^2}{2k_F^2} q^2 dq \sin \theta d\theta d\phi \end{aligned}$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\begin{aligned} \int_0^\pi \delta(\hbar v_k q \cos \theta - \hbar \omega_q) \sin \theta d\theta &= \int_{-1}^1 \frac{1}{\hbar v_F q} \delta\left(x - \frac{\omega_q}{v_F q}\right) dx = \frac{1}{\hbar v_F q} \\ \frac{1}{\tau(\varepsilon_k)} &= \frac{\mathcal{V}}{4\pi^2\hbar} \int_0^{q_D} |M_q|^2 \frac{1}{\hbar v_F q} (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) \frac{q^2}{2k_F^2} q^2 dq \times 2\pi \\ &= \frac{\mathcal{V}}{4\pi\hbar^2 k_F^2 v_F} \int_0^{q_D} |M_q|^2 q^3 (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) dq \end{aligned}$$

Since  $k_F^3 = 3\pi^2 n$

$$\begin{aligned} \frac{1}{\tau(\varepsilon_k)} &= \frac{m\mathcal{V}}{12\pi^3\hbar^3 n} \int_0^{q_D} |M_q|^2 q^3 (2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0) dq \\ 2n_q^0 + 1 - f_{k-q}^0 + f_{k+q}^0 &= \frac{2}{e^{\hbar\omega_q/k_B T} - 1} + 1 - \frac{1}{e^{-\hbar\omega_q/k_B T} + 1} + \frac{1}{e^{\hbar\omega_q/k_B T} + 1} \\ &= \frac{2}{e^{\hbar\omega_q/k_B T} - 1} + \frac{e^{-\hbar\omega_q/k_B T}}{e^{-\hbar\omega_q/k_B T} + 1} + \frac{1}{e^{\hbar\omega_q/k_B T} + 1} \\ &= \frac{2}{e^{\hbar\omega_q/k_B T} - 1} + \frac{2}{e^{\hbar\omega_q/k_B T} + 1} \\ \frac{1}{\tau(\varepsilon_k)} &= \frac{m\mathcal{V}}{6\pi^3\hbar^3 n} \int_0^{q_D} |M_q|^2 q^3 \left( \frac{1}{e^{\hbar\omega_q/k_B T} - 1} + \frac{1}{e^{\hbar\omega_q/k_B T} + 1} \right) dq \end{aligned}$$

(3) For the electron-phonon interaction

$$|M_q|^2 = \frac{2\hbar q^2}{\rho_0 \omega_0 \mathcal{V}} V_0^2$$

$$\frac{1}{\tau(\varepsilon_k)} = \frac{mV_0^2}{3\pi^3 \hbar^2 \rho_0 \omega_0 n} \int_0^{q_D} q^2 q^3 \left( \frac{1}{e^{\hbar\omega_q/k_B T} - 1} + \frac{1}{e^{\hbar\omega_q/k_B T} + 1} \right) dq$$

Let  $x = \hbar\omega_q/k_B T$

$$\begin{aligned}\frac{1}{\tau(\varepsilon_k)} &= \lambda_{\text{el-ph}} \left( \frac{T}{T_D} \right)^5 \int_0^{T_D/T} x^5 \left( \frac{1}{e^x - 1} + \frac{1}{e^x + 1} \right) dx \\ &= \lambda_{\text{el-ph}} \left( \frac{T}{T_D} \right)^5 \int_0^{T_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx\end{aligned}$$

(4) In general

$$\rho(T) = \rho(0) + C \left( \frac{T}{T_D} \right)^\alpha \int_0^{T_D/T} \frac{x^\alpha}{(e^x - 1)(1 - e^{-x})} dx$$

1.  $\alpha = 5$  implies that the resistance is due to scattering of electrons by phonons (as it is for simple metals)
2.  $\alpha = 3$  implies that the resistance is due to s-d electron scattering (as is the case for transition metals)
3.  $\alpha = 2$  implies that the resistance is due to electron-electron interaction.

## C. MATTHEISEN RULE

(1) The phonon and defect scattering mechanism are independent.

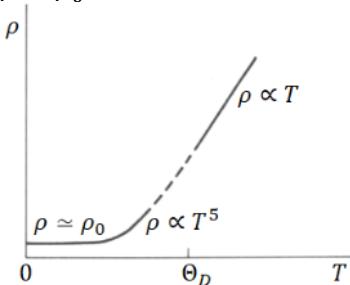
$$\frac{1}{\tau} = \frac{1}{\tau_{\text{phonon}}} + \frac{1}{\tau_{\text{impurity}}} \Rightarrow \rho = \rho_{\text{phonon}} + \rho_{\text{impurity}}$$

(2) At low temperatures, the total theoretical resistivity is

$$\rho = \underbrace{\rho_0}_{\text{impurity}} + \underbrace{aT^2}_{\text{e-e}} + \underbrace{bT^5}_{\text{e-ph}}$$

At high temperature, the resistivity will become

$$\rho = \rho_0 + aT$$



# 7-1 Itinerant Electron Model

Tuesday, December 20, 2011 8:30 PM

## A. BAND STRUCTURE

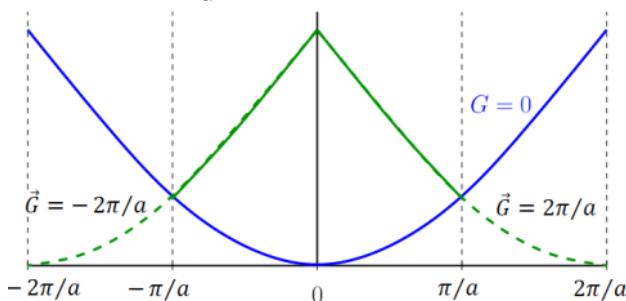
- (1) Central Equation in the first Brillouin zone

$$\left[ \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m} - \varepsilon \right] c_{k-G} + \sum_{G'} V_{G'-G} c_{k-G'} = 0 \quad [\text{c.f.2-2}]$$

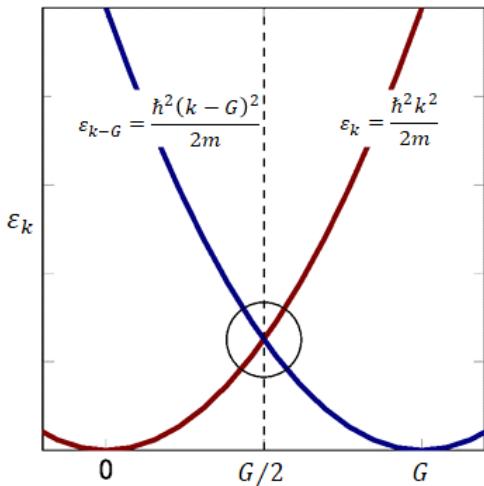
Let  $V_{G'-G} = 0$ , we obtain

$$\left[ \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m} - \varepsilon \right] c_{k-G} = 0$$
$$\varepsilon = \varepsilon_{k-G} = \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m}$$

All parabolic bands of the type  $\varepsilon_{k-G}$  centered around the reciprocal lattice vectors  $\vec{G}$ .



- (2) Near the zone boundary



$$\varepsilon_k = \frac{\hbar^2 (\vec{G}/2 + \delta\vec{k})^2}{2m} \approx \varepsilon_{G/2} + \frac{\hbar^2}{2m} \vec{G} \cdot \delta\vec{k}$$

$$\varepsilon_{k-G} = \frac{\hbar^2 (\vec{G}/2 - \delta\vec{k} - \vec{G})^2}{2m} \approx \varepsilon_{G/2} + \frac{\hbar^2}{2m} \vec{G} \cdot \delta\vec{k}$$

$$\varepsilon_k = \varepsilon_{k-G}$$

### (3) Zone scheme

1. Extended zone scheme:

$$\psi_{k'}(\vec{r}) = \psi_k(\vec{r}) \text{ for } \vec{k} \in 1^{\text{st}} \text{ BZ and } \vec{k}' \notin 1^{\text{st}} \text{ BZ}$$

**PROOF:**

$\vec{k}'$  is outside the 1<sup>st</sup> BZ and  $\vec{k} = \vec{k}' + \vec{G}$  is inside the 1<sup>st</sup> BZ.

$$\psi_{k'}(\vec{r}) = u_{k'}(\vec{r}) e^{i\vec{k}' \cdot \vec{r}} = u_{k'}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} e^{-i\vec{G} \cdot \vec{r}}$$

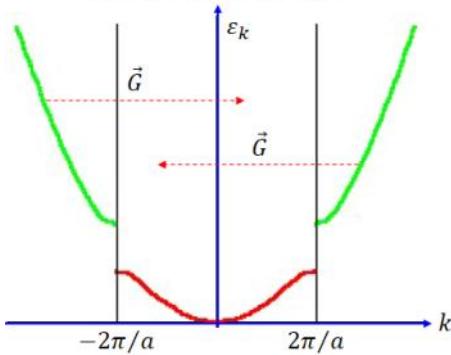
Both  $e^{-i\vec{G} \cdot \vec{r}}$  and  $u_{k'}(\vec{r})$  are lattice-periodic, so is

$$u_k(\vec{r}) \equiv u_{k'}(\vec{r}) e^{-i\vec{G} \cdot \vec{r}}$$

$\Rightarrow \psi_k(\vec{r}) = u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} = \psi_{k'}(\vec{r})$  is a Bloch function

■

### Extended zone scheme



2. Reduced zone scheme:

Band index

$$\left. \begin{aligned} \hat{\mathcal{H}}\psi_k(\vec{r}) &= \varepsilon_k \psi_k(\vec{r}) \\ \hat{\mathcal{H}}\psi_{k'}(\vec{r}) &= \varepsilon_{k'} \psi_{k'}(\vec{r}) \end{aligned} \right\} \Rightarrow \varepsilon_{k'} = \varepsilon_k$$

$\varepsilon_k$  is multi-valued function of  $\vec{k}$ .

Each branch of  $\varepsilon_k$  forms an energy band.

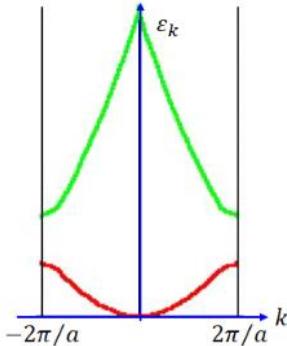
Bloch functions need band index

$$\psi_{nk}(\vec{r}) = u_{nk}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

for  $\vec{k} \in 1^{\text{st}}$  BZ

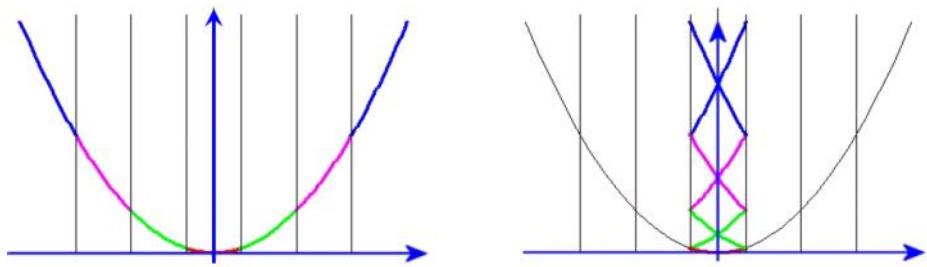
$\Rightarrow \varepsilon_{nk}$  single-valued

### Reduced zone scheme

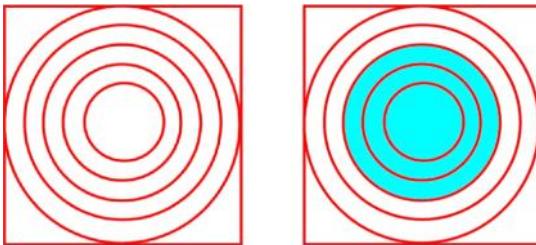


## B. FERMI SURFACE

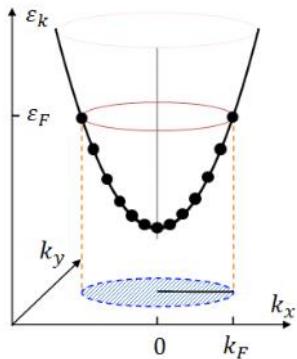
- (1) The constant energy surfaces are circular.



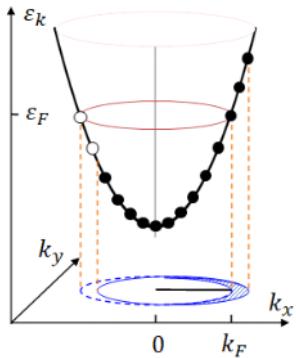
For a monovalent element, the volume of the Fermi surface is half that of the Brillouin zone.



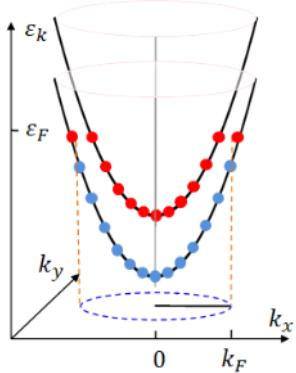
For  $\vec{G} = 0$ :



- (2) In the presence of the electric field:



(3) In the presence of the magnetic field:



## 7-2 Nearly Free Electron Model

Tuesday, December 20, 2011 8:30 PM

### A. NONDEGENERATE PERTURBATION

- (1) Central Equation in the first Brillouin zone

$$\left[ \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m} - \varepsilon \right] c_{k-G} + \sum_{G'} V_{G'-G} c_{k-G'} = 0 \quad [\text{c.f.2-2}]$$

Treat the periodic potential as a weak perturbation

$$V_{G'-G} \rightarrow \lambda V_{G'-G}$$

We shall expand the solution as a Taylor series in  $\lambda$ :

$$c_{k-G} = c_{k-G}^{(0)} + \lambda c_{k-G}^{(1)} + \lambda^2 c_{k-G}^{(2)} + \dots$$

$$\varepsilon = \varepsilon^{(0)} + \lambda \varepsilon^{(1)} + \lambda^2 \varepsilon^{(2)} + \dots$$

- (2) Substituting these expansions into the central equation gives

$$\begin{aligned} & \left( \varepsilon_{k-G}^{(0)} - \varepsilon \right) c_{k-G} + \sum_{G'} V_{G'-G} c_{k-G'} = 0 \\ & \left( \varepsilon_{k-G}^{(0)} - \varepsilon^{(0)} - \lambda \varepsilon^{(1)} - \lambda^2 \varepsilon^{(2)} - \dots \right) \left( c_{k-G}^{(0)} + \lambda c_{k-G}^{(1)} + \lambda^2 c_{k-G}^{(2)} + \dots \right) \\ & + \sum_{G'} \lambda V_{G'-G} \left( c_{k-G'}^{(0)} + \lambda c_{k-G'}^{(1)} + \lambda^2 c_{k-G'}^{(2)} + \dots \right) = 0 \\ & \left( \varepsilon_{k-G}^{(0)} - \varepsilon^{(0)} \right) c_{k-G}^{(0)} + \left[ \left( \varepsilon_{k-G}^{(0)} - \varepsilon^{(0)} \right) c_{k-G}^{(1)} - \varepsilon^{(1)} c_{k-G}^{(0)} + \sum_{G'} V_{G'-G} c_{k-G'}^{(0)} \right] \\ & + O(\lambda^2) + \dots = 0 \end{aligned}$$

- (3) Solve the equation above order by order in  $\lambda$ .

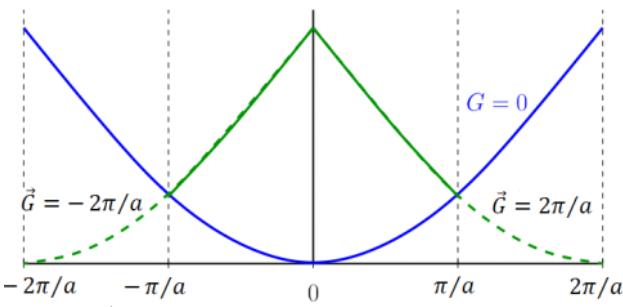
1. Order  $\lambda^0$

$$\left( \varepsilon_{k-G}^{(0)} - \varepsilon^{(0)} \right) c_{k-G}^{(0)} = 0$$

The solutions ( $V_G = 0$  empty lattice) have the form

$$\varepsilon^{(0)} = \varepsilon_{k-G}^{(0)} = \frac{\hbar^2 (\vec{k} - \vec{G})^2}{2m}$$

All parabolic bands of the type  $\varepsilon_{k-G}^{(0)}$  centered around the reciprocal lattice vectors  $\vec{G}$ .



2. Order  $\lambda^1$

$$(\varepsilon_{k-G}^{(0)} - \varepsilon^{(0)}) c_{k-G}^{(1)} - \varepsilon^{(1)} c_{k-G}^{(0)} + \sum_{G'} V_{G'-G} c_{k-G'}^{(0)} = 0$$

(a) For  $\varepsilon^{(0)} = \varepsilon_{k-G}^{(0)}$ , only  $\vec{G}' = \vec{G}$  survives the sum

$$\Rightarrow \varepsilon^{(1)} c_{k-G}^{(0)} = V_0 c_{k-G}^{(0)}$$

$$\Rightarrow \varepsilon^{(1)} = V_0$$

Let  $V_0 = 0 \Rightarrow \varepsilon^{(1)} = 0$

(b) For  $\varepsilon^{(0)} = \varepsilon_k^{(0)}$  and  $\vec{G}' \neq \vec{G}$

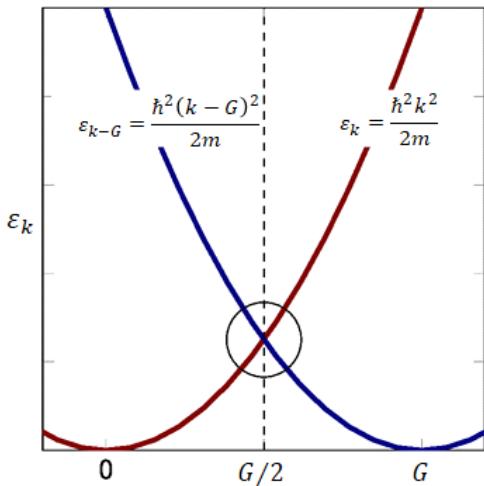
$$c_{k-G}^{(1)} = \sum_{G' \neq G} \frac{V_{G'-G}}{\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}} c_{k-G'}^{(0)}$$

For a fixed  $\vec{k}$  and  $\vec{G}$ , and  $\vec{G}' \neq \vec{G}$ ,  $|\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}| \gg V_{G'-G}$ , we can use nondegenerate perturbation theory.

(4) Failure of non-degenerate perturbation theory

In non-degenerate perturbation theory, the zero-order energy is non-degenerate.

However, near the zone boundary



Free-electron states at the zone boundary  $\vec{k} = \vec{G}/2$

$$\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} \left(\frac{\vec{G}}{2}\right)^2 = \varepsilon_{G/2}^{(0)}$$

$$\varepsilon_{k-G}^{(0)} = \frac{\hbar^2}{2m} \left(\frac{\vec{G}}{2} - \vec{G}\right)^2 = \varepsilon_{G/2}^{(0)}$$

Since  $\varepsilon_k^{(0)} = \varepsilon_{k-G}^{(0)}$ , the zero-order energy states are degenerate.

## B. DEGENERATE PERTURBATION AND ENERGY GAP

- (1) Assume that  $m$  energy levels  $\varepsilon_{k-G_1}^{(0)}, \dots, \varepsilon_{k-G_m}^{(0)}$  are close together within  $V_G$

- For  $\vec{G}' \neq \vec{G}_1, \dots, \vec{G}_m$ , one has

$$c_{k-G}^{(1)} = \sum_{G' \neq G_1 \dots G_m} \frac{V_{G'-G}}{\varepsilon_{k-G}^{(0)} - \varepsilon_{k-G'}^{(0)}} c_{k-G'}^{(0)}$$

- For  $\vec{G}' = \vec{G}_1, \dots, \vec{G}_m$ , one has

$$\begin{aligned} & (\varepsilon_{k-G_i}^{(0)} - \varepsilon) c_{k-G_i} + \sum_{j=1}^m V_{G_j-G_i} c_{k-G_j} + \sum_{G' \neq G_1 \dots G_m} V_{G'-G_i} c_{k-G'} = 0 \\ & \Rightarrow (\varepsilon_{k-G_i}^{(0)} - \varepsilon) c_{k-G_i} + \sum_{j=1}^m V_{G_j-G_i} c_{k-G_j} \\ & \quad + \sum_{G' \neq G_1 \dots G_m} V_{G'-G_i} \sum_{G'' \neq G_1 \dots G_m} \frac{V_{G''-G'}}{\varepsilon_{k-G'}^{(0)} - \varepsilon_{k-G''}^{(0)}} c_{k-G''}^{(0)} = 0 \end{aligned}$$

$$\Rightarrow \left( \varepsilon_{k-G_i}^{(0)} - \varepsilon \right) c_{k-G_i} + \sum_{j=1}^m V_{G_j-G_i} c_{k-G_j} + O(V_G^2) = 0$$

Leading order in  $V_G$

$$\left( \varepsilon_{k-G_i}^{(0)} - \varepsilon \right) c_{k-G_i} + \sum_{j=1}^m V_{G_j-G_i} c_{k-G_j} = 0$$

(2) Suppose  $m = 2$

$$\begin{cases} \left( \varepsilon - \varepsilon_{k-G_1}^{(0)} \right) c_{k-G_1} - V_{G_2-G_1} c_{k-G_2} = 0 \\ \left( \varepsilon - \varepsilon_{k-G_2}^{(0)} \right) c_{k-G_2} - V_{G_1-G_2} c_{k-G_1} = 0 \end{cases}$$

Let  $\vec{q} = \vec{k} - \vec{G}_1$ ,  $\vec{G} = \vec{G}_2 - \vec{G}_1$

$$\begin{cases} \left( \varepsilon - \varepsilon_q^{(0)} \right) c_q - V_G c_{q-G} = 0 \\ \left( \varepsilon - \varepsilon_{q-G}^{(0)} \right) c_{q-G} - V_{-G} c_q = 0 \end{cases}$$

$$\begin{vmatrix} \varepsilon - \varepsilon_q^{(0)} & -V_G \\ -V_G^* & \varepsilon - \varepsilon_{q-G}^{(0)} \end{vmatrix} = 0$$

$$\Rightarrow \left( \varepsilon - \varepsilon_q^{(0)} \right) \left( \varepsilon - \varepsilon_{q-G}^{(0)} \right) - |V_G|^2 = 0$$

$$\Rightarrow \varepsilon^2 - \left( \varepsilon_q^{(0)} + \varepsilon_{q-G}^{(0)} \right) \varepsilon + \varepsilon_q^{(0)} \varepsilon_{q-G}^{(0)} - |V_G|^2 = 0$$

$$\Rightarrow \varepsilon_{\pm} = \frac{1}{2} \left( \varepsilon_q^{(0)} + \varepsilon_{q-G}^{(0)} \right) \pm \frac{1}{2} \sqrt{\left( \varepsilon_q^{(0)} + \varepsilon_{q-G}^{(0)} \right)^2 - 4 \left( \varepsilon_q^{(0)} \varepsilon_{q-G}^{(0)} - |V_G|^2 \right)}$$

$$= \frac{1}{2} \left( \varepsilon_q^{(0)} + \varepsilon_{q-G}^{(0)} \right) \pm \sqrt{\left( \frac{\varepsilon_q^{(0)} - \varepsilon_{q-G}^{(0)}}{2} \right)^2 + |V_G|^2}$$

(3) For  $\vec{q}$  close to 0 (near the zone center)

$$\varepsilon_{q-G}^{(0)} \approx \varepsilon_q^{(0)} = \frac{\hbar^2 |\delta \vec{q}|^2}{2m} = \varepsilon_{\delta q}^{(0)}$$

The free electron approximation, the parabolic band, remains a good approximation near the zone center of the Brillouin zone.

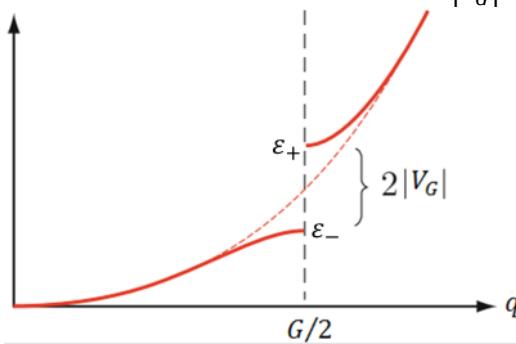
(4) For  $\vec{q}$  close to  $\vec{G}/2$  (near the zone boundary)

$$\text{Let } \vec{q} = \frac{\vec{G}}{2} + \delta \vec{q}$$

$$\begin{aligned}
\varepsilon_q^{(0)} &= \frac{\hbar^2}{2m} \left( \frac{\vec{G}}{2} + \delta \vec{q} \right)^2 = \frac{\hbar^2}{2m} \left| \frac{\vec{G}}{2} \right|^2 + \frac{\hbar^2}{2m} \vec{G} \cdot \delta \vec{q} + \frac{\hbar^2}{2m} |\delta \vec{q}|^2 \\
\varepsilon_{q-G}^{(0)} &= \frac{\hbar^2}{2m} \left( \frac{\vec{G}}{2} + \delta \vec{q} - \vec{G} \right)^2 = \frac{\hbar^2}{2m} \left| \frac{\vec{G}}{2} \right|^2 - \frac{\hbar^2}{2m} \vec{G} \cdot \delta \vec{q} + \frac{\hbar^2}{2m} |\delta \vec{q}|^2 \\
\varepsilon_q^{(0)} + \varepsilon_{q-G}^{(0)} &= 2 \frac{\hbar^2}{2m} \left| \frac{\vec{G}}{2} \right|^2 + 2 \frac{\hbar^2}{2m} |\delta \vec{q}|^2 = 2 (\varepsilon_{G/2}^{(0)} + \varepsilon_{\delta q}^{(0)}) \\
\varepsilon_q^{(0)} - \varepsilon_{q-G}^{(0)} &= 2 \frac{\hbar^2}{2m} \vec{G} \cdot \delta \vec{q} \\
\Rightarrow \varepsilon_+ &= \varepsilon_{G/2}^{(0)} + \varepsilon_{\delta q}^{(0)} + \sqrt{\left( \frac{\hbar^2}{2m} \vec{G} \cdot \delta \vec{q} \right)^2 + |V_G|^2} \\
&\approx \varepsilon_{G/2}^{(0)} + \varepsilon_{\delta q}^{(0)} + |V_G| \left( 1 + \frac{1}{2} \frac{\hbar^4}{4m^2} \frac{G^2 \delta q^2}{|V_G|^2} \right) \\
&= \varepsilon_{G/2}^{(0)} + |V_G| + \frac{\hbar^2 \delta q^2}{2m} + \frac{\hbar^4 G^2 \delta q^2}{8m^2 |V_G|}
\end{aligned}$$

Similarly,

$$\begin{aligned}
\text{Let } \vec{q} &= \frac{\vec{G}}{2} - \delta \vec{q} \\
\Rightarrow \varepsilon_- &\approx \varepsilon_{G/2}^{(0)} + \varepsilon_{\delta q}^{(0)} - |V_G| \left( 1 + \frac{1}{2} \frac{\hbar^4}{4m^2} \frac{G^2 \delta q^2}{|V_G|^2} \right) \\
&= \varepsilon_{G/2}^{(0)} - |V_G| + \frac{\hbar^2 \delta q^2}{2m} - \frac{\hbar^4 G^2 \delta q^2}{8m^2 |V_G|}
\end{aligned}$$



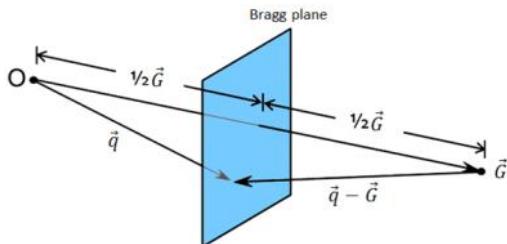
At zone boundary  $\vec{q} = \vec{G}/2$ , the group velocity is zero, i.e.,

$$\frac{\delta \varepsilon_{\pm}}{\delta \vec{q}} = \frac{\hbar^2 \delta \vec{q}}{m} \pm \frac{\hbar^4 G^2 \delta \vec{q}}{4m^2 |V_G|^2} = 0 \Rightarrow \delta \vec{q} = 0$$

$$\Delta\varepsilon = \varepsilon_+ - \varepsilon_- = \left(\varepsilon_{G/2}^{(0)} + |V_G|\right) - \left(\varepsilon_{G/2}^{(0)} - |V_G|\right) = 2|V_G|$$

Every Fourier component of the periodic potential gives rise to a band gap.

- (5) Since  $\vec{q}$  is on the Bragg plane,



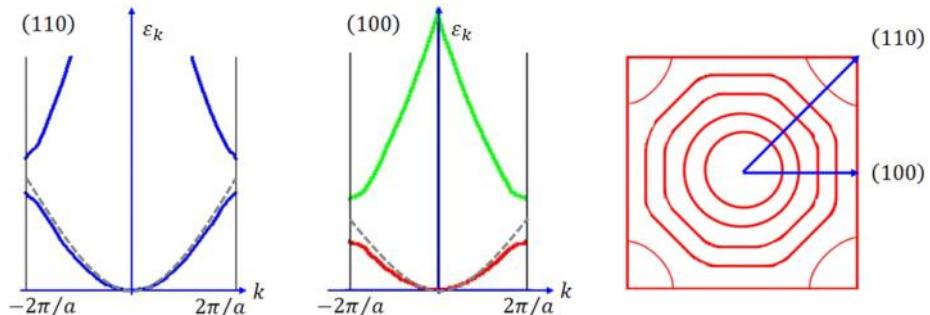
the weak periodic potential has its major effects on only those electron levels whose wave vector are close to the Bragg plane.

Bragg reflection at zone boundaries produce energy gaps (Peierls, 1930).

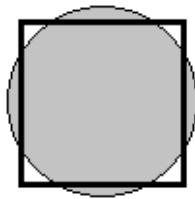
## C. FERMI SURFACE

- (1) Nearly free electrons

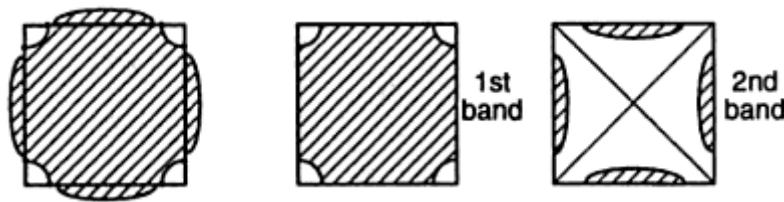
With the crystal potential, the energy inside the first Brillouin zone is lower close to the zone boundary. So the Fermi surface is extended towards the zone boundary as it gets close.



The Fermi surface cross the Brillouin zone boundary of a square lattice.



As a free-electron Fermi surface completely encloses the first Brillouin zone, the portions of the Fermi surface in the second Brillouin zone is mapped back into the first Brillouin zone so that the energy surface is continuous.



- (2) Fermi surface is orthogonal to the zone boundary

$$\varepsilon_{\pm} = \frac{1}{2} (\varepsilon_q^{(0)} + \varepsilon_{q-G}^{(0)}) \pm \sqrt{\left(\frac{\varepsilon_q^{(0)} - \varepsilon_{q-G}^{(0)}}{2}\right)^2 + |V_G|^2}$$

$$\nabla_q \varepsilon_{\pm} = \frac{1}{2} (\nabla_q \varepsilon_q^{(0)} + \nabla_q \varepsilon_{q-G}^{(0)}) \pm \frac{1}{2} 2 \frac{(\varepsilon_q^{(0)} - \varepsilon_{q-G}^{(0)}) (\nabla_q \varepsilon_q^{(0)} - \nabla_q \varepsilon_{q-G}^{(0)})}{\sqrt{\left(\frac{\varepsilon_q^{(0)} - \varepsilon_{q-G}^{(0)}}{2}\right)^2 + |V_G|^2}}$$

At the zone boundary  $\varepsilon_q^{(0)} = \varepsilon_{q-G}^{(0)}$

$$\nabla_q \varepsilon_{\pm} = \frac{\hbar^2}{2m} (\vec{q} + \vec{q} + \vec{G}) \rightarrow \frac{\hbar^2}{m} \left( \frac{\vec{q}}{2} + \vec{G} \right) \cdot \vec{G} = 0$$

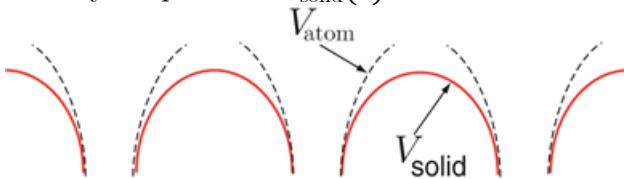
## 7-3 Localized Electron Model

Tuesday, December 20, 2011 8:30 PM

### A. LINEAR COMBINATION OF ATOMIC ORBITALS

#### (1) Crystal Hamiltonian

The crystal potential  $V_{\text{solid}}(\vec{r})$



can be approximated as a sum of atomic potentials

$$V_{\text{solid}}(\vec{r}) = V(\vec{r}) \equiv \sum_{\vec{R}} V_{\text{atom}}(\vec{r} - \vec{R})$$

where  $V_{\text{atom}}(\vec{r} - \vec{R})$  is the potential due to one atom alone and  $\vec{R}$  is the position of the atom.

$$V(\vec{r} - \vec{R}) = \sum_{\vec{R}'} V_{\text{atom}}((\vec{r} - \vec{R}) - \vec{R}') = \sum_{\vec{R}'} V_{\text{atom}}(\vec{r} - (\vec{R} - \vec{R}'))$$

Let  $\vec{R}'' = \vec{R} - \vec{R}'$

$$V(\vec{r} - \vec{R}) = \sum_{\vec{R}''} V_{\text{atom}}(\vec{r} - \vec{R}'') = V(\vec{r})$$

$\Rightarrow V(\vec{r})$  is periodic

In a crystal, the single-particle Hamiltonian can be written as

$$\begin{aligned}\hat{\mathcal{H}} &= \frac{\hat{\mathbf{p}}^2}{2m} + V(\vec{r}) \\ &= \frac{\hat{\mathbf{p}}^2}{2m} + \sum_{\vec{R}} V_{\text{atom}}(\vec{r} - \vec{R}) \\ &= \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} + V_{\text{atom}}(\vec{r} - \vec{R})}_{\hat{\mathcal{H}}_{\text{atom}}} + \underbrace{\sum_{\vec{R} \neq \vec{R}'} V_{\text{atom}}(\vec{r} - \vec{R}')}_{\Delta V(\vec{r})}\end{aligned}$$

where  $\Delta V(\vec{r}) = V(\vec{r}) - V_{\text{atom}}(\vec{r} - \vec{R})$  encodes all the differences between the true potential in the crystal and the potential of an isolated atom.

(2) The single particle states are

$$\hat{\mathcal{H}}\psi(\vec{r}) = [\hat{\mathcal{H}}_{\text{atom}} + \Delta V(\vec{r})]\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

where the Schrödinger equation for an electron in an isolated atom is

$$\hat{\mathcal{H}}_{\text{atom}}\phi(\vec{r}) = \left[ \frac{\hat{p}^2}{2m} + V_{\text{atom}}(\vec{r}) \right] \phi(\vec{r}) = \varepsilon_{\text{atom}}\phi(\vec{r})$$

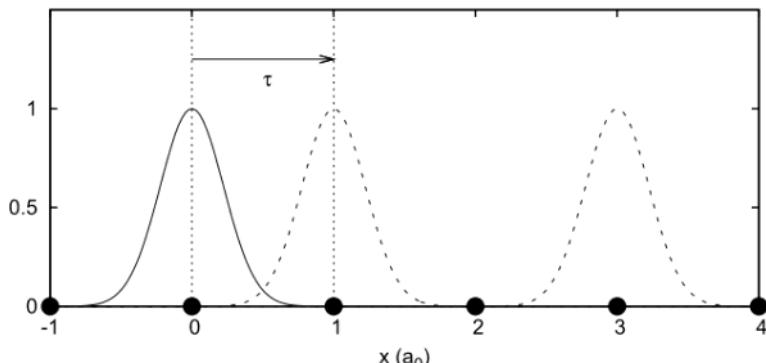
where  $\phi(\vec{r})$  is the atomic orbital (wavefunction).

Assume that the atomic orbitals are localized around one atom, i.e., these wavefunctions decay rapidly away from  $\vec{r} = 0$  and so the overlap integral between wavefunctions located on separate atomic sites in the crystal is small.

$$\begin{aligned} \int \phi^*(\vec{r} - \vec{R}') \phi(\vec{r} - \vec{R}) d^3r &= \int \phi^*(\vec{r} - \vec{R}') \phi(\vec{r} - \vec{R}' - \vec{R}'') d^3r' \\ &= \int \phi^*(\vec{r}') \phi(\vec{r}' - \vec{R}'') d^3r' \\ &\approx \begin{cases} 1, & \vec{R}'' = 0 \\ 0, & \text{otherwise} \end{cases} \end{aligned}$$

### EXAMPLES:

The atomic orbitals in 1D crystal



$$\vec{R}'' = 0, \pm a\hat{x}, \pm 2a\hat{x}, \dots$$

(3) Since

$$\int \phi^*(\vec{r}') \phi(\vec{r}' - \vec{R}'') d^3r' \approx \begin{cases} 1, & \vec{R}'' = 0 \\ 0, & \text{otherwise} \end{cases}$$

a single orbital  $\phi(\vec{r})$  does not obey Bloch's condition.

OS:

$$\text{If } \phi(\vec{r}) \text{ obeys Bloch's condition, i.e., } \phi(\vec{r} - \vec{\mathcal{R}}'') = \phi(\vec{r}) e^{-i\vec{k} \cdot \vec{\mathcal{R}}''}$$

$$\int \phi^*(\vec{r}') \phi(\vec{r}' - \vec{\mathcal{R}}'') d^3 r' = e^{-i\vec{k} \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r}') \phi(\vec{r}') d^3 r'$$

In a periodic potential, a wavefunction must satisfy Bloch's theorem. Thus, we introduce a linear combination of atomic orbitals (LCAO) (John Lennard-Jones, 1929),

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\mathcal{R}} \phi(\vec{r} - \vec{\mathcal{R}}) e^{i\vec{k} \cdot \vec{\mathcal{R}}}$$

where there are  $N$  number of atoms and the factor of  $1/\sqrt{N}$  ensures the Bloch state is normalized.

**PROOF:**

$$\begin{aligned} \hat{T}_{\mathcal{R}'} \psi_k(\vec{r}) &= \psi_k(\vec{r} + \vec{\mathcal{R}}') \\ &= \frac{1}{\sqrt{N}} \sum_{\mathcal{R}} \phi(\vec{r} - \vec{\mathcal{R}} + \vec{\mathcal{R}}') e^{i\vec{k} \cdot \vec{\mathcal{R}}} \\ &= e^{i\vec{k} \cdot \vec{\mathcal{R}}'} \frac{1}{\sqrt{N}} \sum_{\mathcal{R}} \phi(\vec{r} - (\vec{\mathcal{R}} - \vec{\mathcal{R}}')) e^{i\vec{k} \cdot (\vec{\mathcal{R}} - \vec{\mathcal{R}}')} \\ &= \psi_k(\vec{r}) e^{i\vec{k} \cdot \vec{\mathcal{R}}'} \\ \psi_k(\vec{r}) &= \frac{1}{\sqrt{N}} \sum_{\mathcal{R}} \phi(\vec{r} - \vec{\mathcal{R}}) e^{i\vec{k} \cdot \vec{\mathcal{R}}} \\ &= \frac{1}{\sqrt{N}} \sum_{\mathcal{R}} e^{i\vec{k} \cdot \vec{\mathcal{R}}} \frac{1}{\sqrt{N}} \sum_G \phi_G e^{i\vec{G} \cdot (\vec{r} - \vec{\mathcal{R}})} \\ &= \frac{1}{N} \sum_G \phi_G \sum_{\mathcal{R}} e^{i(\vec{k} - \vec{G}) \cdot \vec{\mathcal{R}}} e^{i\vec{G} \cdot \vec{r}} = \frac{1}{N} \sum_G \phi_{k-G} \sum_{\mathcal{R}} e^{i\vec{G} \cdot \vec{\mathcal{R}}} e^{i(\vec{k} - \vec{G}) \cdot \vec{r}} \\ &= \sum_G \phi_{k-G} e^{i(\vec{k} - \vec{G}) \cdot \vec{r}} \\ &= u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \end{aligned}$$

■

(4) Normalization of LCAO wavefunction

$$\langle \psi_{k'} | \psi_k \rangle = \frac{1}{N} \sum_{\mathcal{R}\mathcal{R}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

Consider,

$$\begin{aligned}\frac{1}{N} \sum_{\vec{\mathcal{R}}\vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} &= \frac{1}{N} \sum_{\vec{\mathcal{R}}\vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}' + \vec{k}' \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}})} \\ &= \frac{1}{N} \sum_{\vec{\mathcal{R}}\vec{\mathcal{R}}'} e^{i(\vec{k} - \vec{k}') \cdot \vec{\mathcal{R}}} e^{i\vec{k}' \cdot (\vec{\mathcal{R}} - \vec{\mathcal{R}}')}\end{aligned}$$

Let  $\vec{\mathcal{R}}'' = \vec{\mathcal{R}} - \vec{\mathcal{R}}'$

$$\frac{1}{N} \sum_{\vec{\mathcal{R}}\vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} = \frac{1}{N} \sum_{\vec{\mathcal{R}}} e^{i(\vec{k} - \vec{k}') \cdot \vec{\mathcal{R}}} \sum_{\vec{\mathcal{R}}''} e^{i\vec{k}' \cdot \vec{\mathcal{R}}''} = \delta_{k,k'} \sum_{\vec{\mathcal{R}}''} e^{i\vec{k}' \cdot \vec{\mathcal{R}}''}$$

$$\begin{aligned}\langle \psi_{k'} | \psi_k \rangle &= \delta_{k,k'} \sum_{\vec{\mathcal{R}}''} e^{i\vec{k}' \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r \\ &= \delta_{k,k'} \sum_{\vec{\mathcal{R}}''} e^{i\vec{k}' \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \phi(\vec{r} - \vec{\mathcal{R}}' - \vec{\mathcal{R}}'') d^3 r \\ &= \delta_{k,k'} \sum_{\vec{\mathcal{R}}''} e^{i\vec{k}' \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r}') \phi(\vec{r}' - \vec{\mathcal{R}}'') d^3 r' \\ &= \begin{cases} \delta_{k,k'}, & \vec{\mathcal{R}}'' = 0 \\ 0, & \text{otherwise} \end{cases}\end{aligned}$$

## B. ENERGY BAND OF ONE ORBITAL

- (1) Assume that a crystal has one atom in the unit cell and where only one atomic orbital  $\phi(\vec{r})$  contribute to the crystal states.

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{\mathcal{R}}} \phi(\vec{r} - \vec{\mathcal{R}}) e^{i\vec{k} \cdot \vec{\mathcal{R}}}$$

The energy of a state  $\psi_k(\vec{r})$  is given by

$$\varepsilon_k = \frac{\langle \psi_k | \hat{H} | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle}$$

- (2) Energy band  $\varepsilon_k$

Since  $\langle \psi_k | \psi_k \rangle = 1$

$$\varepsilon_k = \frac{\langle \psi_k | \hat{H} | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} = \langle \psi_k | \hat{H} | \psi_k \rangle$$

Calculating

$$\langle \psi_{k'} | \hat{H} | \psi_k \rangle = \frac{1}{N} \sum_{\vec{\mathcal{R}} \vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') [\hat{\mathcal{H}}_{\text{atom}}(\vec{\mathcal{R}}) + \Delta V(\vec{r})] \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

Since

$$\hat{\mathcal{H}}_{\text{atom}} \phi(\vec{r}) = \left[ \frac{\hat{p}^2}{2m} + V_{\text{atom}}(\vec{r}) \right] \phi(\vec{r}) = \varepsilon_{\text{atom}} \phi(\vec{r})$$

$$\langle \psi_{k'} | \hat{H} | \psi_k \rangle$$

$$= \varepsilon_{\text{atom}} \frac{1}{N} \sum_{\vec{\mathcal{R}} \vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

$$+ \frac{1}{N} \sum_{\vec{\mathcal{R}} \vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \Delta V(\vec{r}) \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

$$= \varepsilon_{\text{atom}} \langle \psi_{k'} | \psi_k \rangle + \frac{1}{N} \sum_{\vec{\mathcal{R}} \vec{\mathcal{R}}'} e^{i(\vec{k} \cdot \vec{\mathcal{R}} - \vec{k}' \cdot \vec{\mathcal{R}}')} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \Delta V(\vec{r}) \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

$$= \varepsilon_{\text{atom}} \langle \psi_{k'} | \psi_k \rangle + \delta_{k,k'} \sum_{\vec{\mathcal{R}}''} e^{i\vec{k}' \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \Delta V(\vec{r}) \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

$$\varepsilon_k = \langle \psi_k | \hat{H} | \psi_k \rangle$$

$$= \varepsilon_{\text{atom}} \langle \psi_k | \psi_k \rangle + \sum_{\vec{\mathcal{R}}''} e^{i\vec{k} \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \Delta V(\vec{r}) \phi(\vec{r} - \vec{\mathcal{R}}) d^3 r$$

$$= \varepsilon_{\text{atom}} + \sum_{\vec{\mathcal{R}}''} e^{i\vec{k} \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r} - \vec{\mathcal{R}}') \Delta V(\vec{r} - \vec{\mathcal{R}}') \phi(\vec{r} - \vec{\mathcal{R}}' - \vec{\mathcal{R}}'') d^3 r$$

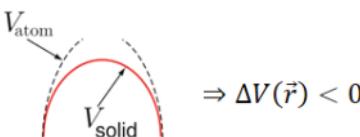
$$= \varepsilon_{\text{atom}} + \sum_{\vec{\mathcal{R}}''} e^{i\vec{k} \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r}') \Delta V(\vec{r}') \phi(\vec{r}' - \vec{\mathcal{R}}'') d^3 r'$$

(3) We classify the sum over  $\vec{\mathcal{R}}''$  according to the distance between two atoms:

1. zero distance  $\vec{\mathcal{R}}'' = 0$

$$\begin{aligned} & \sum_{\vec{\mathcal{R}}''} e^{i\vec{k} \cdot \vec{\mathcal{R}}''} \int \phi^*(\vec{r}') \Delta V(\vec{r}') \phi(\vec{r}' - \vec{\mathcal{R}}'') d^3 r' \\ &= \int \phi^*(\vec{r}') \Delta V(\vec{r}') \phi(\vec{r}') d^3 r' \end{aligned}$$

Since  $V_{\text{atom}} > V_{\text{solid}}$



$$\Rightarrow \Delta V(\vec{r}) < 0$$

Define  $\alpha = - \int \phi^*(\vec{r}') \Delta V(\vec{r}') \phi(\vec{r}') d^3 r' = \text{constant} > 0$

2. nearest neighbor distance  $\vec{R}'' = a$

$$\sum_{\vec{R}''} e^{i\vec{k} \cdot \vec{R}''} \int \phi^*(\vec{r}') \Delta V(\vec{r}') \phi(\vec{r}' - \vec{R}'') d^3 r'$$

$$\text{Define } \gamma = - \int \phi^*(\vec{r}') \Delta V(\vec{r}') \phi(\vec{r}' - a) d^3 r'$$

OS:

Empirically, we do not attempt to evaluate the overlap integral. Instead we adjust to match experiments.

$$\Rightarrow \varepsilon_k = \varepsilon_{\text{atom}} - \alpha - \gamma \sum_{\vec{R}''} e^{i\vec{k} \cdot \vec{R}''} = -\gamma \sum_{\vec{R}''} e^{i\vec{k} \cdot \vec{R}''} - \mu$$

where  $\mu = \alpha - \varepsilon_{\text{atom}}$

This is the energy band of tight-binding method.

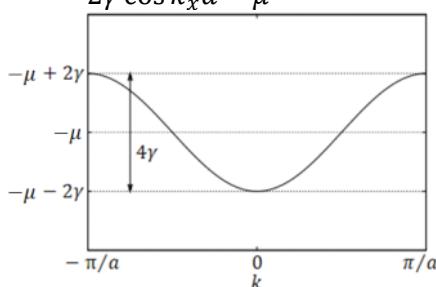
EXAMPLES:

1. One atomic orbital in the unit cell in 1D crystal



There are 2 nearest neighbors:  $\vec{R}'' = \pm a\hat{x}$

$$\begin{aligned} \varepsilon_k &= -\gamma \sum_{\vec{R}''} e^{i\vec{k} \cdot \vec{R}''} - \mu \\ &= -\gamma (e^{i\vec{k} \cdot a\hat{x}} + e^{-i\vec{k} \cdot a\hat{x}}) - \mu \\ &= -2\gamma \cos k_x a - \mu \end{aligned}$$



OS:

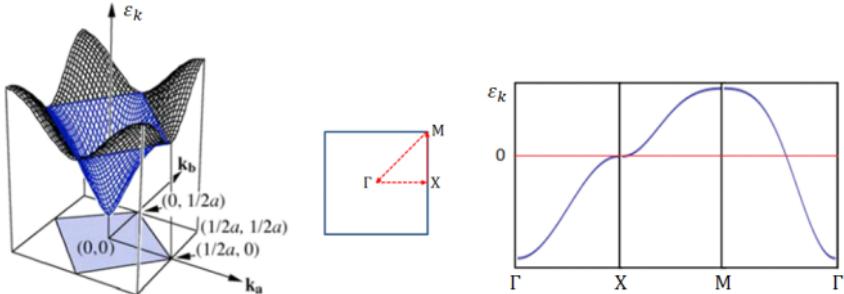
The bands width  $4\gamma$  depends upon the degree of overlap in the atomic orbitals from which they arise.

2. One atomic orbital in the unit cell in 2D crystal  
 There are 4 nearest neighbors:  $\vec{R}'' = \pm a\hat{x}$  and  $\pm a\hat{y}$

$$\sum_{\vec{R}''} e^{i\vec{k}\cdot\vec{R}''} = e^{i\vec{k}\cdot a\hat{x}} + e^{-i\vec{k}\cdot a\hat{x}} + e^{i\vec{k}\cdot a\hat{y}} + e^{-i\vec{k}\cdot a\hat{y}}$$

$$= 2 \cos k_x a + 2 \cos k_y a$$

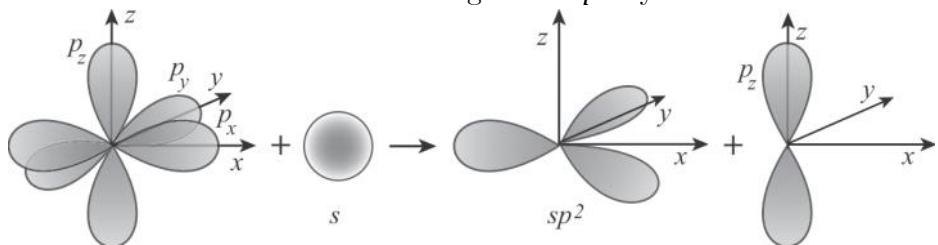
$$\varepsilon_k = -2\gamma(\cos k_x a + \cos k_y a) - \mu$$



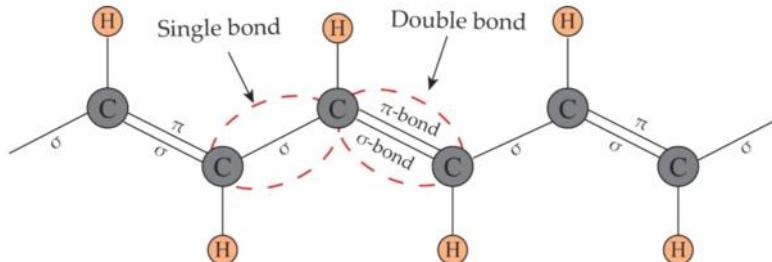
### C. ENERGY BAND OF TWO ORBITALS

- (1) Polyacetylene [pali-Uh-set-1-een]

The carbon atom has the electronic configuration  $[1s^2 2s^2 2p^2]$ . In conjugated polymers the two  $p$  orbitals in the  $xy$  plane (i.e.,  $p_x$  and  $p_y$ ) will combine with the  $2s$  orbital to give an  $sp^2$  hybridization.

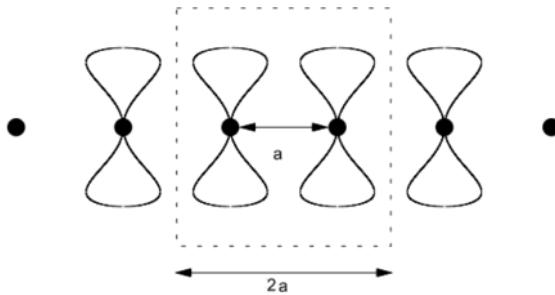


The structure of polyacetylene: the backbone contains conjugated double bonds.



(2) Average bond model:

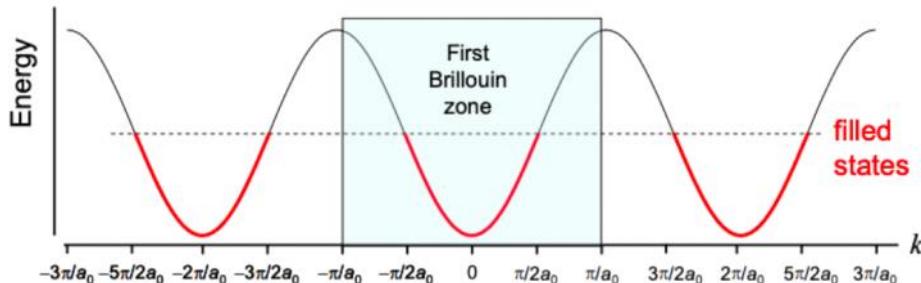
The unit cell of polyacetylene under the average bond model has only a single carbon atom. Each carbon atom contributes a single  $p$ -orbital,



The LCAO wavefunction

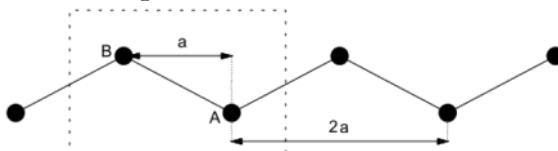
$$\Phi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\mathcal{R}} \phi(\vec{r} - \vec{\mathcal{R}}) e^{i\vec{k}\cdot\vec{\mathcal{R}}}$$

$$\varepsilon_k = \langle \Phi_k | \hat{H} | \Phi_k \rangle = -\gamma \sum_{\mathcal{R}''} e^{i\vec{k}\cdot\vec{\mathcal{R}}''} - \mu = -2\gamma \cos 2k_x a - \mu$$



The band of states is only half full

(3) Alternating bond model:



The LCAO wavefunction

$$\Phi_{\alpha k}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\mathcal{R}_\alpha} \phi(\vec{r} - \vec{\mathcal{R}}_\alpha) e^{i\vec{k}\cdot\vec{\mathcal{R}}_\alpha}$$

where  $\alpha = A$  and  $B$  atoms in the unit cell.

The crystal wavefunctions are

$$\psi_k(\vec{r}) = \sum_{\alpha} c_{\alpha k} \Phi_{\alpha k}(\vec{r})$$

Considering  $\alpha = A$  and  $B$  in turn, we get two equations:

$$\langle \Phi_{Ak} | \hat{H} | \psi_k \rangle = \sum_{\beta} c_{\beta k} \langle \Phi_{Ak} | \hat{H} | \Phi_{\beta k} \rangle = \sum_{\beta} c_{\beta k} \varepsilon_k \langle \Phi_{Ak} | \Phi_{\beta k} \rangle$$

$$\langle \Phi_{Bk} | \hat{H} | \psi_k \rangle = \sum_{\beta} c_{\beta k} \langle \Phi_{Bk} | \hat{H} | \Phi_{\beta k} \rangle = \sum_{\beta} c_{\beta k} \varepsilon_k \langle \Phi_{Bk} | \Phi_{\beta k} \rangle$$

where

$\langle \Phi_{Ak} | \hat{H} | \Phi_{Ak} \rangle$  and  $\langle \Phi_{Bk} | \hat{H} | \Phi_{Bk} \rangle$  indicate the hopping between two unit cells.

$\langle \Phi_{Ak} | \hat{H} | \Phi_{Bk} \rangle$  and  $\langle \Phi_{Bk} | \hat{H} | \Phi_{Ak} \rangle$  indicate the hopping inside a unit cell.

Thus,

$$c_{Ak} \langle \Phi_{Ak} | \hat{H} | \Phi_{Ak} \rangle + c_{Bk} \langle \Phi_{Ak} | \hat{H} | \Phi_{Bk} \rangle = c_{Ak} \varepsilon_k \langle \Phi_{Ak} | \Phi_{Ak} \rangle = c_{Ak} \varepsilon_k$$

$$c_{Ak} \langle \Phi_{Bk} | \hat{H} | \Phi_{Ak} \rangle + c_{Bk} \langle \Phi_{Bk} | \hat{H} | \Phi_{Bk} \rangle = c_{Bk} \varepsilon_k \langle \Phi_{Bk} | \Phi_{Bk} \rangle = c_{Bk} \varepsilon_k$$

$$\text{Let } h_{\alpha\beta} = \langle \Phi_{\alpha k} | \hat{H} | \Phi_{\beta k} \rangle$$

$$\begin{pmatrix} h_{AA} & h_{AB} \\ h_{BA} & h_{BB} \end{pmatrix} \begin{pmatrix} c_{Ak} \\ c_{Bk} \end{pmatrix} = \varepsilon_k \begin{pmatrix} c_{Ak} \\ c_{Bk} \end{pmatrix}$$

$$\text{where } h_{AB} = h_{BA}^*$$

OS:

The equations above can be rewritten in a matrix form.

$$\mathbf{c} = \begin{pmatrix} c_{Ak} \\ c_{Bk} \end{pmatrix}$$

$$\mathbf{H} = \begin{pmatrix} h_{AA} & h_{AB} \\ h_{BA} & h_{BB} \end{pmatrix}$$

$$\mathbf{H} \cdot \mathbf{c} = \varepsilon_k \mathbf{c} \Rightarrow \begin{pmatrix} h_{AA} & h_{AB} \\ h_{BA} & h_{BB} \end{pmatrix} \begin{pmatrix} c_{Ak} \\ c_{Bk} \end{pmatrix} = \varepsilon_k \begin{pmatrix} c_{Ak} \\ c_{Bk} \end{pmatrix}$$

The secular equation is

$$\begin{vmatrix} h_{AA} - \varepsilon_k & h_{AB} \\ h_{BA} & h_{BB} - \varepsilon_k \end{vmatrix} = 0$$

$$\Rightarrow (h_{AA} - \varepsilon_k)(h_{BB} - \varepsilon_k) - h_{AB}h_{BA} = 0$$

$$\Rightarrow \varepsilon_k^2 - (h_{AA} + h_{BB})\varepsilon_k + h_{AA}h_{BB} - |h_{AB}|^2 = 0$$

$$\Rightarrow \varepsilon_k^{\pm} = -\frac{1}{2}(h_{AA} + h_{BB}) \pm \sqrt{\frac{1}{4}(h_{AA} - h_{BB})^2 + |h_{AB}|^2}$$

With 2 atoms in the unit cell, we get 2 valid solutions at each  $k$ , i.e. 2

bands.

$$h_{AA} = \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}'_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}'_A)} \int \phi^*(\vec{r} - \vec{\mathcal{R}}'_A) \hat{\mathcal{H}} \phi(\vec{r} - \vec{\mathcal{R}}_A) d^3r$$

Since

$$\begin{aligned} \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}'_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}'_A)} &= \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}'_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}'_A)} e^{i(\vec{k}' \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_A)} \\ &= \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}'_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_A)} e^{i(\vec{k}' \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}'_A)} \end{aligned}$$

$$\text{Let } \vec{\mathcal{R}}_{AA} = \vec{\mathcal{R}}_A - \vec{\mathcal{R}}'_A = (2a, 0)$$

$$\begin{aligned} \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}'_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}'_A)} &= \frac{1}{N} \sum_{\vec{\mathcal{R}}_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_A)} \sum_{\vec{\mathcal{R}}_{AA}} e^{i\vec{k}' \cdot \vec{\mathcal{R}}_{AA}} \\ &= \delta_{k,k'} \sum_{\vec{\mathcal{R}}_{AA}} e^{i\vec{k}' \cdot \vec{\mathcal{R}}_{AA}} \end{aligned}$$

$$\begin{aligned} h_{AA} &= \sum_{\vec{\mathcal{R}}_{AA}} e^{i\vec{k} \cdot \vec{\mathcal{R}}_{AA}} \int \phi^*(\vec{r} - \vec{\mathcal{R}}'_A) \hat{\mathcal{H}} \phi(\vec{r} - (\vec{\mathcal{R}}'_A + \vec{\mathcal{R}}_{AA})) d^3r \\ &= \sum_{\vec{\mathcal{R}}_{AA}} e^{i\vec{k} \cdot \vec{\mathcal{R}}_{AA}} \int \phi^*(\vec{r}') \hat{\mathcal{H}} \phi(\vec{r}' - \vec{\mathcal{R}}_{AA}) d^3r' \end{aligned}$$

Since polyacetylene is a 1D crystal and  $\vec{k}$  is in the  $x$ -direction.

$$h_{AA} = (e^{i\vec{k} \cdot 2a\hat{x}} + e^{-i\vec{k} \cdot 2a\hat{x}})(-\gamma) = -2\gamma \cos 2k_x a$$

$$h_{AB} = \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}_B} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_B)} \int \phi^*(\vec{r} - \vec{\mathcal{R}}_B) \hat{\mathcal{H}} \phi(\vec{r} - \vec{\mathcal{R}}_A) d^3r$$

Since

$$\begin{aligned} \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}_B} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_B)} &= \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}_B} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_B)} e^{i(\vec{k}' \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_A)} \\ &= \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}_B} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_A)} e^{i(\vec{k}' \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_B)} \end{aligned}$$

$$\text{Let } \vec{\mathcal{R}}_{AB} = \vec{\mathcal{R}}_A - \vec{\mathcal{R}}_B = \left(a, \frac{a}{\sqrt{3}}\right)$$

$$\begin{aligned} \frac{1}{N} \sum_{\vec{\mathcal{R}}_A \vec{\mathcal{R}}_B} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_B)} &= \frac{1}{N} \sum_{\vec{\mathcal{R}}_A} e^{i(\vec{k} \cdot \vec{\mathcal{R}}_A - \vec{k}' \cdot \vec{\mathcal{R}}_A)} \sum_{\vec{\mathcal{R}}_{AB}} e^{i\vec{k}' \cdot \vec{\mathcal{R}}_{AB}} \\ &= \delta_{k,k'} \sum_{\vec{\mathcal{R}}_{AB}} e^{i\vec{k}' \cdot \vec{\mathcal{R}}_{AB}} \end{aligned}$$

$$\begin{aligned}
h_{AB} &= \sum_{\vec{\mathcal{R}}_{AB}} e^{i\vec{k}\cdot\vec{\mathcal{R}}_{AB}} \int \phi^*(\vec{r} - \vec{\mathcal{R}}_B) \hat{\mathcal{H}} \phi\left(\vec{r} - (\vec{\mathcal{R}}_B + \vec{\mathcal{R}}_{AB})\right) d^3r \\
&= \sum_{\vec{\mathcal{R}}_{AB}} e^{i\vec{k}\cdot\vec{\mathcal{R}}_{AB}} \int \phi^*(\vec{r}') \hat{\mathcal{H}} \phi\left(\vec{r}' - \vec{\mathcal{R}}_{AB}\right) d^3r'
\end{aligned}$$

Since polyacetylene is a 1D crystal and  $\vec{k}$  is in the  $x$ -direction.

$$h_{AB} = (e^{i\vec{k}\cdot a\hat{x}} + e^{-i\vec{k}\cdot a\hat{x}})(-\gamma) = -2\gamma \cos k_x a$$

Since

$$h_{AA} = h_{BB} = -2\gamma \cos 2k_x a$$

$$h_{AB} = h_{BA} = -2\gamma \cos k_x a$$

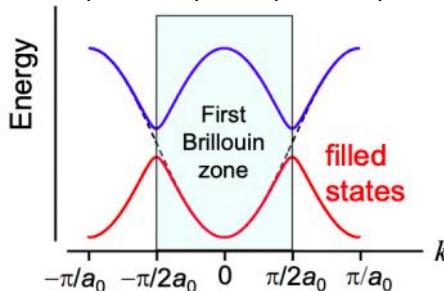
$$\varepsilon_k^\pm = -\frac{1}{2}(h_{AA} + h_{BB}) \pm \sqrt{\frac{1}{4}(h_{AA} - h_{BB})^2 + |h_{AB}|^2}$$

$$= -h_{AA} \pm \sqrt{|h_{AB}|^2}$$

$$= 2\gamma \cos 2k_x a \pm 2\gamma \cos k_x a$$

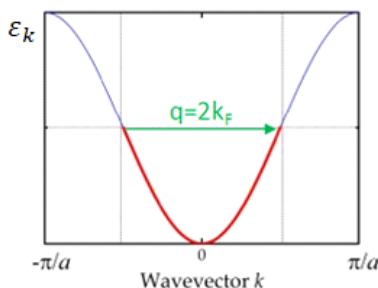
Band gap at  $k_x = \pi/a$ :

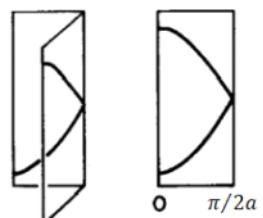
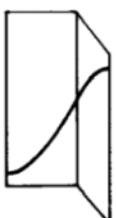
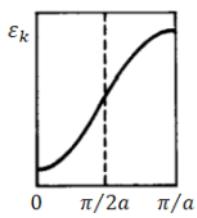
$$\Delta\varepsilon_k = |\varepsilon_k^+ - \varepsilon_k^-| = 4\gamma |\cos k_x a| = 4\gamma$$



OS:

Band folding





# 7-4 Wannier Wavefunction

Tuesday, December 20, 2011      8:30 PM

## A. WANNIER [Wannier] FUNCTIONS (1937)

- (1) A Bloch function  $\psi_k(\vec{r})$  is periodic in  $\vec{k}$  by reciprocal lattice vector  $\vec{G}$ , can be expressed by a Fourier representation with non-zero coefficients only for Bravais-lattice vectors  $\vec{R}_i$ .

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_i w(\vec{r}, \vec{R}_i) e^{i\vec{k} \cdot \vec{R}_i}$$

where the Fourier coefficients are called Wannier function.

- (2) Since

$$\begin{aligned} w(\vec{r}, \vec{R}_i) &= \frac{1}{\sqrt{N}} \sum_k \psi_k(\vec{r}) e^{-i\vec{k} \cdot \vec{R}_i} \\ &= \frac{1}{\sqrt{N}} \sum_k u_k(\vec{r}) e^{i\vec{k} \cdot \vec{r}} e^{-i\vec{k} \cdot \vec{R}_i} \\ &= \frac{1}{\sqrt{N}} \sum_k u_k(\vec{r}) e^{i\vec{k} \cdot (\vec{r} - \vec{R}_i)} \\ &= \frac{1}{\sqrt{N}} \sum_k u_k(\vec{r} - \vec{R}_i) e^{i\vec{k} \cdot (\vec{r} - \vec{R}_i)} \dots\dots(a) \\ &\equiv w(\vec{r} - \vec{R}_i) \end{aligned}$$

⇒ The Wannier function depends only on the difference  $\vec{r} - \vec{R}_i$ .

- (3) From equation (a), we have

$$w(\vec{r} - \vec{R}_i) = \frac{1}{\sqrt{N}} \sum_k u_k(\vec{r} - \vec{R}_i) e^{i\vec{k} \cdot (\vec{r} - \vec{R}_i)}$$

Using periodic boundary condition  $u_k(\vec{r} + N_l \vec{a}_l) = u_k(\vec{r})$

$$\begin{aligned}
w(\vec{r} + N_l \vec{a}_l - \vec{R}_i) &= \frac{1}{\sqrt{N}} \sum_k u_k (\vec{r} + N_l \vec{a}_l - \vec{R}_i) e^{i\vec{k} \cdot (\vec{r} + N_l \vec{a}_l - \vec{R}_i)} \\
&= \frac{1}{\sqrt{N}} \sum_k u_k (\vec{r} - \vec{R}_i) e^{i\vec{k} \cdot (\vec{r} - \vec{R}_i)} e^{i\vec{k} \cdot N_l \vec{a}_l} \\
&= w(\vec{r} - \vec{R}_i)
\end{aligned}$$

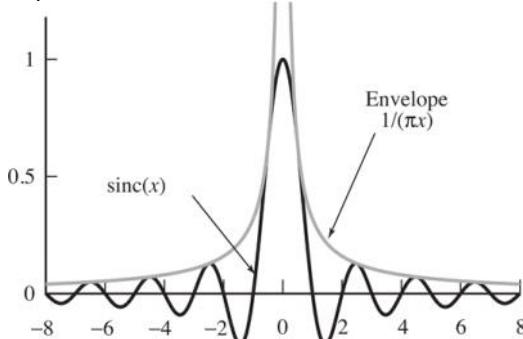
$$\Rightarrow e^{-i\vec{k} \cdot N_l \vec{a}_l} = 1$$

$$\Rightarrow k_l = \frac{2\pi m_l}{N_l a_l} \text{ where } m_l = 0, \dots, N_l - 1$$

Considering the case  $|\vec{R}_i| = a_1$

$$w(x - a_1) = \frac{1}{\sqrt{N}} \sum_{m_1} u_k (x - a_1) e^{im_1 \frac{2\pi}{N_1 a_1} (x - a_1)}$$

$$\sum_{m_1} e^{im_1 \frac{2\pi}{N_1 a_1} (x - a_1)} \underset{N_1 \gg 1}{\approx} \frac{\sin(\pi(x - a_1)/a_1)}{\pi(x - a_1)/a_1} = \text{sinc}\left((x - a_1)/a_1\right)$$



$$w(x - a_1) \xrightarrow[a_1 \rightarrow 0]{\frac{1}{\sqrt{N}}} u(x - a_1) \delta(x - a_1)$$

$$= \begin{cases} 0, & x \neq a_1 \\ \frac{1}{\sqrt{N}} u(x - a_1), & x = a_1 \end{cases}$$

$\Rightarrow$  Wannier function is a localized function centered on the real-space lattice site  $\vec{R}_i$ .

$$(4) \text{ Let } |w_i\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-i\vec{k} \cdot \vec{R}_i} |\psi_k\rangle$$

$$\langle w_i | w_j \rangle = \frac{1}{N} \sum_{kk'} e^{i(\vec{k} \cdot \vec{R}_i - \vec{k}' \cdot \vec{R}_j)} \langle \psi_k | \psi_{k'} \rangle = \frac{1}{N} \sum_k e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} = \delta_{ij}$$

$\Rightarrow$  Wannier function is orthonormal.

$$\sum_i |w_i\rangle\langle w_i| = \mathbb{1}$$

$\Rightarrow$  Wannier function is completeness.

$\Rightarrow$  Wannier functions form a set of basis.

### (5) (Optional) Peierls [Pei-erls/pay-earls] substitution

Quantum treatment of magnetic field  $\vec{H} = \nabla \times \vec{A}$

$$\hbar\vec{k} \rightarrow \hbar\vec{k} + \frac{e}{c}\vec{A}$$

$$\Rightarrow \hat{H} = \frac{1}{2m} \left( \hat{p} + \frac{e}{c}\vec{A} \right)^2 + V(\vec{r})$$

The gauge-invariance of the Schrödinger equation requires us to transform the wavefunction amplitude at a site as

$$\begin{aligned} |\tilde{w}_i\rangle &= e^{i\phi_i} |w_i\rangle, \quad \phi_i = -\frac{e}{\hbar c} \int_{R_i}^r \vec{A} \cdot d\vec{l} \\ \hat{H}|\tilde{w}_i\rangle &= \left[ \frac{1}{2m} \left( \hat{p} + \frac{e}{c}\vec{A} \right)^2 + V(\vec{r}) \right] e^{-i\frac{e}{\hbar c} \int_{R_i}^r \vec{A} \cdot d\vec{l}} |w_i\rangle \\ &= e^{-i\frac{e}{\hbar c} \int_{R_i}^r \vec{A} \cdot d\vec{l}} \left[ \frac{1}{2m} \left( \hat{p} + \frac{e}{c}\vec{A} - \frac{e}{c}\vec{A} \right)^2 + V(\vec{r}) \right] |w_i\rangle \\ &= e^{i\phi_i} \left[ \frac{\hat{p}^2}{2m} + V(\vec{r}) \right] |w_i\rangle \end{aligned}$$

$$\tilde{t}_{ij} = \langle \tilde{w}_i | \hat{H} | \tilde{w}_j \rangle_{i \neq j} = \int e^{-i\phi_i} \langle w_i | \frac{\hat{p}^2}{2m} + V(\vec{r}) | w_j \rangle e^{i\phi_j} d^3 r$$

where

$$\phi_i - \phi_j = -\frac{e}{\hbar c} \int_{R_i}^r \vec{A} \cdot d\vec{l} - \left( -\frac{e}{\hbar c} \int_{R_j}^r \vec{A} \cdot d\vec{l} \right) = -\frac{e}{\hbar c} \int_{R_i \rightarrow r \rightarrow R_j} \vec{A} \cdot d\vec{l}$$

To include magnetic fields in lattice model, the integration path is chosen to be the shortest distance over nearest neighbor bond.

$$\begin{aligned} \Rightarrow \phi_i - \phi_j &= -\frac{e}{\hbar c} \int_{R_i \rightarrow r \rightarrow R_j \rightarrow R_i} \vec{A} \cdot d\vec{l} - \left( -\frac{e}{\hbar c} \int_{R_i}^{R_j} \vec{A} \cdot d\vec{l} \right) \\ &= -\frac{e}{\hbar c} \oint \vec{A} \cdot d\vec{l} - \left( -\frac{e}{\hbar c} \int_{R_i}^{R_j} \vec{A} \cdot d\vec{l} \right) \\ &= \Phi - \phi_{ij} \\ \Rightarrow \tilde{t}_{ij} &= t_{ij} e^{-i(\Phi - \phi_{ij})} \end{aligned}$$

Since  $\vec{A}(\vec{r})$  is assumed approximately uniform at the lattice scale,  $\Phi \approx 0$

$$\Rightarrow \tilde{t}_{ij} = t_{ij} e^{i\phi_{ij}}, \quad \phi_{ij} = -\frac{e}{\hbar c} \int_{R_i}^{R_j} \vec{A} \cdot d\vec{l}$$

$\Rightarrow$  Peierls substitution for lattices

## B. ENERGY BAND OF ONE ATOM IN A UNIT CELL

- (1) The tight-binding Hamiltonian is

$$\hat{H} = \sum_{ij} |w_i\rangle \langle w_i| \hat{H} |w_j\rangle \langle w_j| = \sum_{ij} \langle w_i | \hat{H} | w_j \rangle |w_i\rangle \langle w_j|$$

where the matrix elements are

$$\langle w_i | \hat{H} | w_j \rangle = \int w^*(\vec{r} - \vec{R}_i) \hat{\mathcal{H}} w(\vec{r} - \vec{R}_j) d^3 r$$

$$\text{let } \vec{R}_{ij} = \vec{R}_i - \vec{R}_j$$

$$= \int w^*(\vec{r} - \vec{R}_{ij}) \hat{\mathcal{H}} w(\vec{r}) d^3 r$$

1. For  $\vec{R}_{ij} = 0$ , i.e.  $i = j$

$$\text{Define } \mu = - \int w^*(\vec{r}) \hat{\mathcal{H}} w(\vec{r}) d^3 r = \text{constant} > 0$$

$$\langle w_i | \hat{H} | w_j \rangle = -\mu \delta_{ij}$$

$\mu$  is close to the atomic eigenvalue and plays the role of a reference energy.

2. For  $\vec{R}_{ij} \neq 0$

$$\text{Define } t_{ij} = - \int w^*(\vec{r} - \vec{R}_{ij}) \hat{\mathcal{H}} w(\vec{r}) d^3 r > 0$$

$t_{ij}$  is called the hopping integral (or just hopping), and can be viewed as a kinetic energy due to tunneling across a potential barrier between two lattice sites.  $t_{ij}$  depends only on the distance between sites  $\vec{R}_{ij}$ .

$$\Rightarrow \hat{H} = - \sum_{ij} t_{ij} |w_i\rangle \langle w_j| - \mu \sum_i |w_i\rangle \langle w_i|$$

Let  $\hat{c}_i^\dagger$  and  $\hat{c}_i$  be the creation and annihilation operators on lattice site  $\vec{R}_i$ .

$$|w_i\rangle \langle w_j| \text{ maps state on site } \vec{R}_j \text{ onto the state on site } \vec{R}_i$$

→ electron hops from site  $\vec{R}_j$  to site  $\vec{R}_i$

→  $\hat{c}_i^\dagger \hat{c}_j$

$|w_i\rangle\langle w_i|$  = maps state on site  $\vec{R}_i$  onto the state on site  $\vec{R}_i$

→ electron hops from site  $\vec{R}_i$  to site  $\vec{R}_i$

→  $\hat{c}_i^\dagger \hat{c}_i$

$$\Rightarrow \hat{H} = - \sum_{ij} t_{ij} \hat{c}_i^\dagger \hat{c}_j - \sum_i \mu \hat{c}_i^\dagger \hat{c}_i$$

## (2) Diagonalization

$$\hat{c}_i^\dagger = \frac{1}{\sqrt{N}} \sum_k \hat{c}_k^\dagger e^{-i\vec{k} \cdot \vec{R}_i}$$

$$\hat{c}_i = \frac{1}{\sqrt{N}} \sum_k \hat{c}_k e^{i\vec{k} \cdot \vec{R}_i}$$

$$\begin{aligned} \hat{H} &= - \sum_{ij} t_{ij} \frac{1}{\sqrt{N}} \sum_k \hat{c}_k^\dagger e^{-i\vec{k} \cdot \vec{R}_i} \frac{1}{\sqrt{N}} \sum_{k'} \hat{c}_{k'} e^{i\vec{k}' \cdot \vec{R}_j} \\ &\quad - \sum_i \mu \frac{1}{\sqrt{N}} \sum_k \hat{c}_k^\dagger e^{-i\vec{k} \cdot \vec{R}_i} \frac{1}{\sqrt{N}} \sum_{k'} \hat{c}_{k'} e^{i\vec{k}' \cdot \vec{R}_i} \end{aligned}$$

$$\begin{aligned} &= - \sum_{kk'} \hat{c}_k^\dagger \hat{c}_{k'} \frac{1}{N} \sum_{ij} t_{ij} e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_i} e^{i\vec{k}' \cdot (\vec{R}_j - \vec{R}_i)} \\ &\quad - \sum_{kk'} \hat{c}_k^\dagger \hat{c}_{k'} \frac{1}{N} \mu \sum_i e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_i} \end{aligned}$$

Let  $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$  and  $t_{ij} = t$

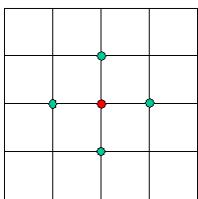
$$= -t \sum_{kk'} \hat{c}_k^\dagger \hat{c}_{k'} \sum_j e^{-i\vec{k}' \cdot \vec{R}_{ij}} \delta_{kk'} - \mu \sum_{kk'} \hat{c}_k^\dagger \hat{c}_{k'} \delta_{kk'}$$

$$= -t \sum_k \hat{c}_k^\dagger \hat{c}_k \sum_j e^{-i\vec{k} \cdot \vec{R}_{ij}} - \mu \sum_k \hat{c}_k^\dagger \hat{c}_k$$

$$= \sum_k \varepsilon_k \hat{c}_k^\dagger \hat{c}_k$$

$$\text{where } \varepsilon_k = -t \sum_j e^{-i\vec{k} \cdot \vec{R}_{ij}} - \mu$$

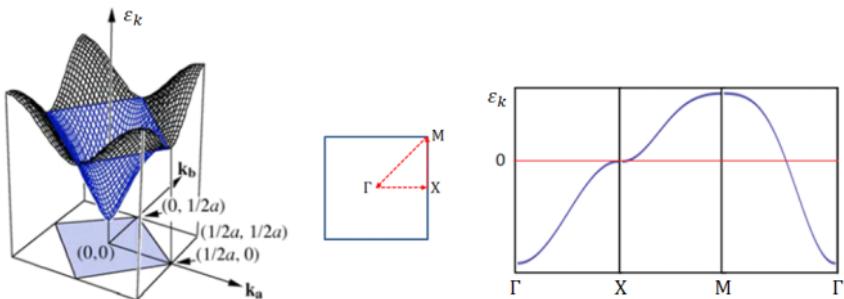
## (3) Monovalent square lattice



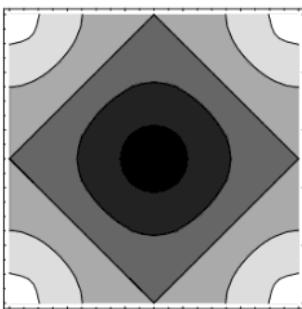
There are 4 nearest-neighbor hopping:  $j = i \pm a\hat{x}$  or  $i \pm a\hat{y}$

### 1. Energy band:

$$\varepsilon_k = -t \sum_j e^{-i\vec{k} \cdot \vec{R}_{ij}} - \mu = -2t(\cos k_x a + \cos k_y a) - \mu$$



### 2. Fermi surface:



$$\varepsilon_k = \text{constant}$$

(a) Near  $\Gamma = (0,0)$  point

$$\varepsilon_k \approx -2t \left( 1 - \frac{1}{2}k_x^2 a^2 + 1 - \frac{1}{2}k_y^2 a^2 \right) - \mu = \text{constant}$$

$$\Rightarrow k_x^2 + k_y^2 = \text{constant}$$

The constant energy contour is a circle.

(b) Near  $M = (\pi/a, \pi/a)$  point

$$\varepsilon_k \approx -2t \left( 1 - \frac{1}{2}(k_x \pm \pi/a)^2 a^2 + 1 - \frac{1}{2}(k_y \pm \pi/a)^2 a^2 \right) - \mu$$

$$= \text{constant}$$

$$\Rightarrow (k_y \pm \pi/a)^2 + (k_y \pm \pi/a)^2 = \text{constant}$$

The constant energy contour breaks into four disjoint components which encircle the corners of the M point.

- (c) Half filling:

$$\varepsilon_k = -2t(\cos k_x a + \cos k_y a)$$

The Fermi surface flattens out along the diagonal directions.

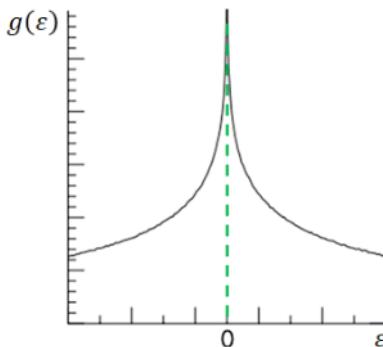


#### GRAPHICALLY PROOF:

The band filling is the ratio of the surface area enclosed by the Fermi surface to the area of the complete Brillouin zone. The square Fermi surface for  $\mu = 0$  corresponds to a half-filled band. ■

3. Density of states (DOS):

$$\begin{aligned} \varepsilon_k &= -2t(\cos k_x a + \cos k_y a) \\ g(\varepsilon) &= \frac{1}{(2\pi)^2} \int \delta(\varepsilon_k - \varepsilon) d^2 k \\ &= \frac{1}{(2\pi)^2} \int \int_{-\infty}^{\infty} e^{-i\alpha(\varepsilon_k - \varepsilon)} \frac{d\alpha}{2\pi} d^2 k \\ &= \frac{1}{(2\pi)^2} \int \int_{-\infty}^{\infty} e^{i\alpha[\varepsilon + 2t(\cos k_x a + \cos k_y a)]} \frac{d\alpha}{2\pi} d^2 k \\ &= \int_{-\infty}^{\infty} e^{i\alpha\varepsilon} \frac{d\alpha}{2\pi} \cdot \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i2t\alpha \cos k_x a} dk_x \cdot \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i2t\alpha \cos k_y a} dk_y \\ &= \int_{-\infty}^{\infty} \frac{1}{a^2} J_0^2(2t\alpha) e^{i\alpha\varepsilon} \frac{d\alpha}{2\pi} \\ &= \frac{1}{a^2} \frac{1}{\pi} \int_0^{\infty} J_0^2(2t\alpha) \cos \alpha\varepsilon d\alpha \end{aligned}$$



Large density of states near the Fermi energy (logarithmic divergent)

$$g(\varepsilon) \approx \ln\left(\frac{\varepsilon}{4t}\right)$$

The singularities occur as  $|\nabla_k \varepsilon_k| = 0$ ,

$$\nabla_k \varepsilon_k = -2ta(\sin k_x a + \sin k_y a) = 0$$

$\vec{k} = (0, 0) \rightarrow \Gamma$  point

$\vec{k} = \left(\pm \frac{\pi}{a}, \pm \frac{\pi}{a}\right) \rightarrow M$  point

$\vec{k} = \left(0, \pm \frac{\pi}{a}\right)$  or  $\left(\pm \frac{\pi}{a}, 0\right) \rightarrow X$  point (saddle point)

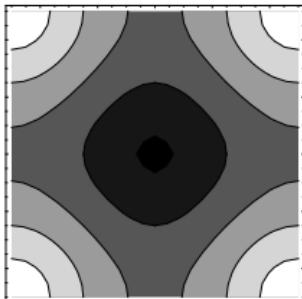
(4) Monovalent square lattice with next nearest-neighbor hopping:

If next nearest-neighbor hopping  $t' > 0$

Energy band:

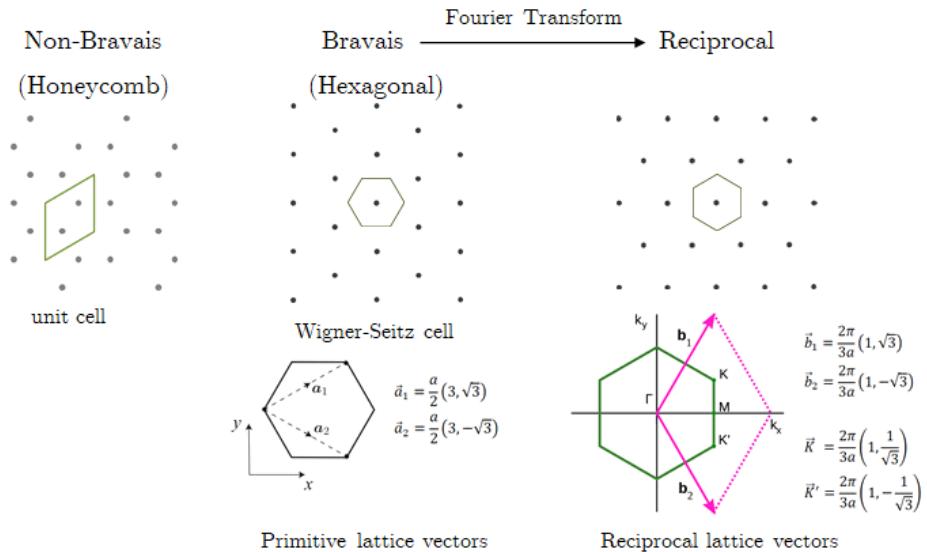
$$\begin{aligned} \varepsilon_k &= -t \sum_j e^{-i\vec{k} \cdot \vec{R}_{ij}} + t' \sum_{j'} e^{-i\vec{k} \cdot \vec{R}_{ij'}} - \mu \\ &= -2t(\cos k_x a + \cos k_y a) + 4t' \cos k_x a \cos k_y a - \mu \end{aligned}$$

Fermi surface:

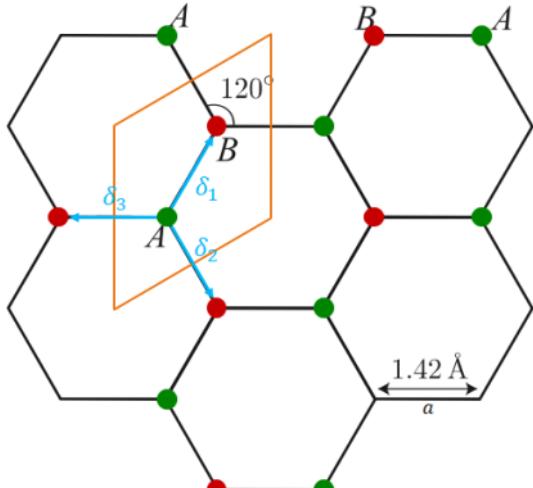


## C. ENERGY BAND OF TWO ATOMS IN A UNIT CELL —GRAPHENE—

(1) Crystal properties:



(2) Electronic properties:



The nearest-neighbor tight-binding Hamiltonian is

$$\hat{H} = - \sum_{ij} t (\hat{a}_i^\dagger \hat{b}_j + \text{H.c.})$$

where  $\hat{a}_i^\dagger$  ( $\hat{b}_i^\dagger$ ) is the creation operator for an electron on the A(B) sublattice.

Take the Fourier transformation:

$$\begin{aligned}\hat{a}_i &= \frac{1}{\sqrt{N}} \sum_k \hat{a}_k e^{i\vec{k} \cdot \vec{R}_i} \\ \hat{a}_i^\dagger &= \frac{1}{\sqrt{N}} \sum_k \hat{a}_k^\dagger e^{-i\vec{k} \cdot \vec{R}_i} \\ \hat{H} &= -\frac{1}{N} \sum_{ij} t \sum_{kk'} \hat{a}_k^\dagger \hat{b}_{k'} e^{-i\vec{k} \cdot \vec{R}_i} e^{i\vec{k}' \cdot \vec{R}_j} + \text{H.c.} \\ &= -t \sum_{kk'} \hat{a}_k^\dagger \hat{b}_{k'} \frac{1}{N} \sum_{ij} e^{-i\vec{k} \cdot \vec{R}_i} e^{i\vec{k}' \cdot (\vec{R}_i + \vec{\delta}_j)} + \text{H.c.} \\ &= -t \sum_k \hat{a}_k^\dagger \hat{b}_k \sum_{j=1}^3 e^{i\vec{k} \cdot \vec{\delta}_j} + \text{H.c.} \\ &= \sum_k \begin{pmatrix} \hat{a}_k^\dagger & \hat{b}_k^\dagger \end{pmatrix} \begin{pmatrix} 0 & h_k \\ h_k^* & 0 \end{pmatrix} \begin{pmatrix} \hat{a}_k \\ \hat{b}_k \end{pmatrix}\end{aligned}$$

where

$$h_k = -t \sum_{j=1}^3 e^{i\vec{k} \cdot \vec{\delta}_j}$$

OS:

Define an operator with two components as

$$\hat{\Psi}_k = \begin{pmatrix} \hat{a}_k \\ \hat{b}_k \end{pmatrix}$$

The Hamiltonian can be written in terms of  $\hat{\Psi}_k$  and  $\hat{\Psi}_k^\dagger$  as,

$$\hat{H} = \sum_k \hat{\Psi}_k^\dagger \begin{pmatrix} 0 & h_k \\ h_k^* & 0 \end{pmatrix} \hat{\Psi}_k = \sum_k \hat{\Psi}_k^\dagger \mathbf{h}_k \hat{\Psi}_k$$

Since the matrix  $\mathbf{h}_k$  is a Hermitian, we can diagonalize  $\mathbf{h}_k$  using a unitary matrix  $\mathbf{U}$ , such that

$$\mathbf{U}^\dagger \cdot \mathbf{h} \cdot \mathbf{U} = \begin{pmatrix} \varepsilon_k^+ & 0 \\ 0 & \varepsilon_k^- \end{pmatrix}$$

Defining

$$\mathbf{U}^\dagger \hat{\Psi}_k = \begin{pmatrix} \hat{c}_{k+} \\ \hat{c}_{k-} \end{pmatrix} \Rightarrow \hat{\Psi}_k = \mathbf{U} \begin{pmatrix} \hat{c}_{k+} \\ \hat{c}_{k-} \end{pmatrix}$$

we can diagonalize the Hamiltonian

$$\begin{aligned}\hat{H} &= \sum_k \begin{pmatrix} \hat{c}_{k+}^\dagger & \hat{c}_{k-}^\dagger \end{pmatrix} \mathbf{U}^\dagger \cdot \mathbf{h} \cdot \mathbf{U} \begin{pmatrix} \hat{c}_{k+} \\ \hat{c}_{k-} \end{pmatrix} \\ &= \sum_k \begin{pmatrix} \hat{c}_{k+}^\dagger & \hat{c}_{k-}^\dagger \end{pmatrix} \begin{pmatrix} \varepsilon_k^+ & 0 \\ 0 & \varepsilon_k^- \end{pmatrix} \begin{pmatrix} \hat{c}_{k+} \\ \hat{c}_{k-} \end{pmatrix} \\ &= \sum_k \varepsilon_k^+ \hat{c}_{k+}^\dagger \hat{c}_{k+} + \varepsilon_k^- \hat{c}_{k-}^\dagger \hat{c}_{k-}\end{aligned}$$

Thus, we can also solve the secular equation to obtain the eigenenergies

$$\begin{vmatrix} -\varepsilon_k & h_k \\ h_k^* & -\varepsilon_k \end{vmatrix} = 0$$

$$\Rightarrow \varepsilon_k^2 - h_k^* h_k = 0$$

$$\Rightarrow \varepsilon_k^\pm = \pm \sqrt{h_k^* h_k}$$

Three nearest-neighbors of an A-sublattice atom are

$$\vec{\delta}_1 = \frac{a}{2}(1, \sqrt{3})$$

$$\vec{\delta}_2 = \frac{a}{2}(1, -\sqrt{3})$$

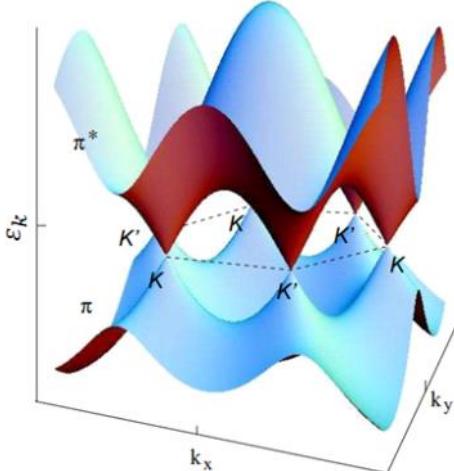
$$\vec{\delta}_3 = a(-1, 0)$$

$$\begin{aligned}h_k &= -t \sum_{j=1}^3 e^{i\vec{k} \cdot \vec{\delta}_j} \\ &= -t \left( e^{i(k_x a/2 + \sqrt{3}k_y a/2)} + e^{i(k_x a/2 - \sqrt{3}k_y a/2)} + e^{i(-k_x a)} \right) \\ &= -te^{-ik_x a} \left( e^{i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + 1 \right)\end{aligned}$$

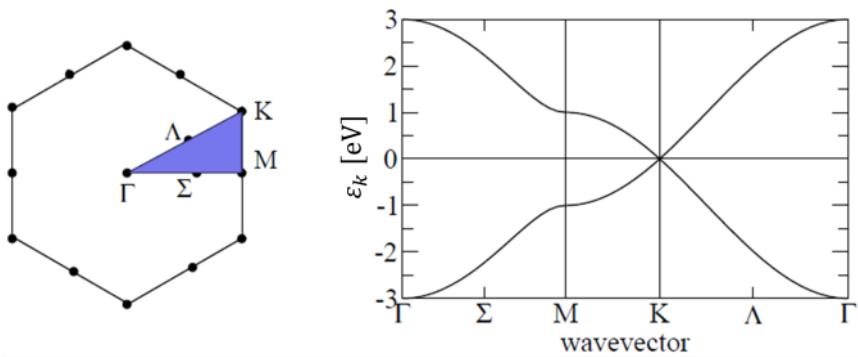
The energy band is

$$\begin{aligned}\varepsilon_k^\pm &= \pm \sqrt{h_k^* h_k} \\ &= \pm \sqrt{t^2 \left( e^{-i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + 1 \right) \left( e^{i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + 1 \right)} \\ &= \pm \sqrt{4 \cos^2 \frac{\sqrt{3}k_y a}{2} + e^{i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + e^{-i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + 1} \\ &= \pm \sqrt{4 \cos^2 \frac{\sqrt{3}k_y a}{2} + 4 \cos \frac{3k_x a}{2} \cos \frac{\sqrt{3}k_y a}{2} + 1}\end{aligned}$$

Full band structure over the whole Brillouin zone



Conventionally plotted band structure



### (3) Dirac point

1. The upper band and lower band touch at K point.

$$\varepsilon_k^+ = \varepsilon_k^- = 0$$

$$h_k = 0 \Rightarrow e^{i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + 1 = 0 \Rightarrow e^{i3k_x a/2} \cos \frac{\sqrt{3}k_y a}{2} = -\frac{1}{2}$$

Since  $e^{i3k_x a/2}$  must be a real number,  $e^{i3k_x a/2} = \pm 1$

$$\text{Choose } e^{i3k_x a/2} = -1 \text{ and } \cos \frac{\sqrt{3}k_y a}{2} = \frac{1}{2}$$

$$\Rightarrow k_x = \frac{2\pi}{3a}, k_y = \frac{2\pi}{3a} \frac{1}{\sqrt{3}}$$

$$\Rightarrow \vec{K} = \frac{2\pi}{3a} \left( 1, \frac{1}{\sqrt{3}} \right)$$

2. For  $\vec{k}$  close to  $\vec{K}$  point

$$\text{Let } \vec{q} = \vec{k} - \vec{K}$$

$$\begin{aligned} h_{K+q} - h_K &= \vec{q} \cdot \nabla_k h_K \Big|_{k=K} \\ &= -te^{-iK_x a} \vec{q} \cdot \nabla_k \left[ e^{i3k_x a/2} 2 \cos \frac{\sqrt{3}k_y a}{2} + 1 \right]_{k=K} \\ &\approx -\frac{3ta}{2} e^{-iK_x a} (iq_x - q_y) \end{aligned}$$

Extract an overall constant factor  $-ie^{-iK_x a}$

$$h_q = \hbar v_F (q_x + iq_y), \quad v_F \equiv \frac{3ta}{2\hbar} \approx 10^6 \text{ m/s}$$

Similarly,

$$h_q^* = \hbar v_F (q_x - iq_y)$$

The Hamiltonian becomes

$$\hat{\mathcal{H}} = \hbar v_F \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} \equiv \hbar v_F \hat{\sigma} \cdot \vec{q}$$

The secular equations is

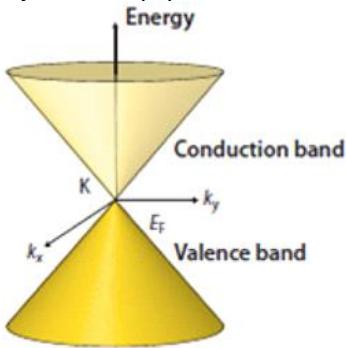
$$\begin{vmatrix} -\varepsilon_q & \hbar v_F (q_x - iq_y) \\ \hbar v_F (q_x + iq_y) & -\varepsilon_q \end{vmatrix} = 0$$

$$\Rightarrow \varepsilon_q^2 - \hbar^2 v_F^2 (q_x - iq_y)(q_x + iq_y) = 0$$

$$\Rightarrow \varepsilon_q^2 - \hbar^2 v_F^2 (q_x^2 + q_y^2) = 0$$

The eigenvalues are a function only of the magnitude of  $\vec{q}$

$$\varepsilon_q = \pm \hbar v_F |\vec{q}|$$



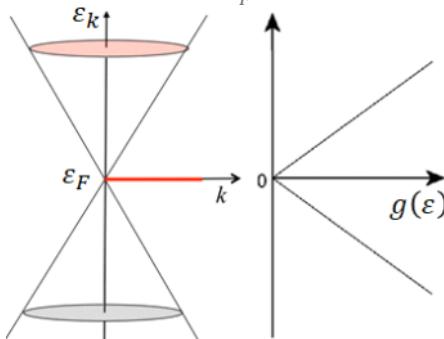
3. Density of states (DOS)

$$\begin{aligned}
g(\varepsilon) &= 2 \times 2 \frac{1}{(2\pi)^2} \int \delta(E_q - E) d^2 q \\
&= 2 \times 2 \frac{1}{(2\pi)^2} 2\pi \int_0^\infty \delta(E_q - E) q dq \\
\varepsilon_q &= \hbar v_F q \Rightarrow d\varepsilon_q = \hbar v_F dq \\
g(\varepsilon) &= \frac{2}{\pi} \int_0^\infty \delta(\varepsilon_q - \varepsilon) \frac{\varepsilon_q}{\hbar v_F} \frac{d\varepsilon_q}{\hbar v_F} = \frac{2\varepsilon}{\pi \hbar^2 v_F^2}
\end{aligned}$$

OS:

$$g(k)dk = 2 \times 2 \times \left( \frac{L^2}{4\pi^2} \times 2\pi k dk \right) / L^2 = \frac{2}{\pi} \frac{\varepsilon}{\hbar^2 v_F^2} d\varepsilon = g(\varepsilon) d\varepsilon$$

$$g(\varepsilon) = \frac{2\varepsilon}{\pi \hbar^2 v_F^2}$$



### -PEIERLS TRANSITION (1955)-

- (1) Monovalent 1D crystal (one atom per unit cell)



The nearest-neighbor tight-binding Hamiltonian is

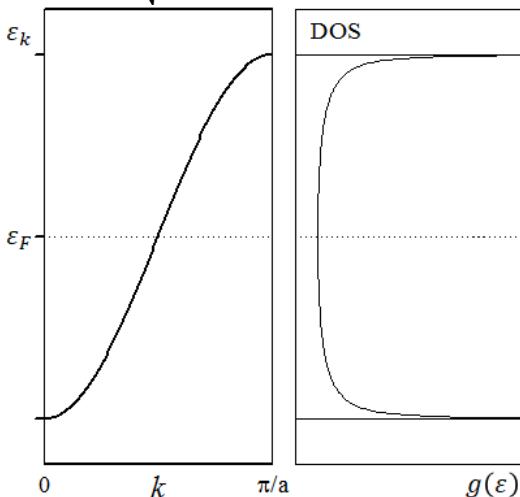
$$\begin{aligned}
\mathcal{H} &= -t \sum_i a_i^\dagger a_{i+1} - t \sum_i a_i^\dagger a_{i-1} \\
&= -t \sum_k a_k^\dagger a_k (e^{i\vec{k} \cdot \vec{a}} + e^{-i\vec{k} \cdot \vec{a}}) \\
&= \sum_k \varepsilon_k a_k^\dagger a_k
\end{aligned}$$

Energy band:

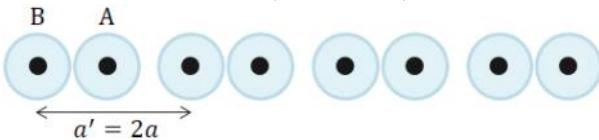
$$\varepsilon_k = -2t \cos k_x a$$

Density of states (DOS):

$$\begin{aligned} g(\varepsilon_k) &= \frac{1}{\pi} \frac{1}{|d\varepsilon_k/dk_x|} \\ &= \frac{1}{\pi} \frac{1}{2t} \frac{1}{a \sin(k_x a)} \\ &= \frac{1}{\pi 2ta} \frac{1}{\sqrt{1 - \varepsilon_k^2/4t^2}} \\ &= \frac{1}{\pi a} \frac{1}{\sqrt{4t^2 - \varepsilon_k^2}} \end{aligned}$$



(2) Lattice deformation (distortion)



The Hamiltonian becomes

$$\begin{aligned}
\mathcal{H} &= -(t + \epsilon) \sum_i a_i^\dagger b_i - (t - \epsilon) \sum_i a_i^\dagger b_{i+1} + \text{h.c.} \\
&= -(t + \epsilon) \sum_i \frac{1}{N} \sum_{kk'} a_k^\dagger b_{k'} e^{-i\vec{k} \cdot \vec{R}_i} e^{i\vec{k}' \cdot (\vec{R}_i - \vec{a} + \vec{\delta})} \\
&\quad - (t - \epsilon) \sum_i \frac{1}{N} \sum_{kk'} a_k^\dagger b_{k'} e^{-i\vec{k} \cdot \vec{R}_i} e^{i\vec{k}' \cdot (\vec{R}_i + \vec{a} + \vec{\delta})} \\
&= -(t + \epsilon) \sum_k a_k^\dagger b_k e^{i\vec{k} \cdot (-\vec{a} + \vec{\delta})} - (t - \epsilon) \sum_k a_k^\dagger b_k e^{i\vec{k} \cdot (\vec{a} + \vec{\delta})} \\
&= \sum_k \psi_k^\dagger \begin{pmatrix} 0 & h_k \\ h_k^* & 0 \end{pmatrix} \psi_k
\end{aligned}$$

where

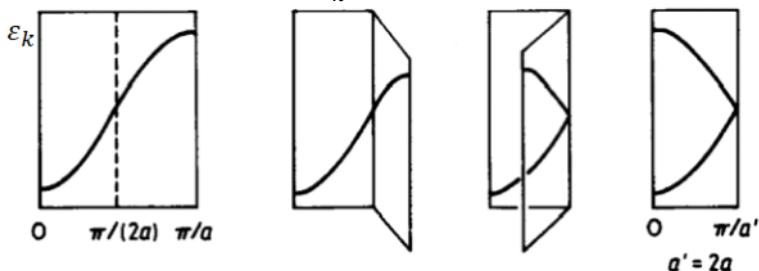
$$h_k = - \left\{ (t + \epsilon) e^{i\vec{k} \cdot (-\vec{a} + \vec{\delta})} + (t - \epsilon) e^{i\vec{k} \cdot (\vec{a} + \vec{\delta})} \right\}$$

Energy band:

$$\begin{aligned}
\varepsilon_k^\pm &= \pm \sqrt{h_k^* h_k} \\
&= \pm \sqrt{2t^2 + 2\epsilon^2 + (t^2 - \epsilon^2) (e^{-2i\vec{k} \cdot \vec{a}} + e^{2i\vec{k} \cdot \vec{a}})} \\
&= \pm \sqrt{2t^2 + 2\epsilon^2 + 2(t^2 - \epsilon^2) \cos 2k_x a} \\
&= \pm \sqrt{2t^2 + 2\epsilon^2 + 2(t^2 - \epsilon^2) \cos k_x a'}
\end{aligned}$$

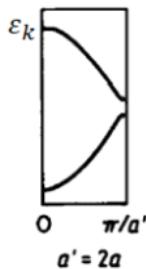
1. If  $\epsilon = 0$

$$\begin{aligned}
\varepsilon_k^\pm &= \pm \sqrt{2t^2 + 2t^2 \cos k_x a'} \\
\text{At } k_x = \pi/a' &= \pi/2a \Rightarrow E_k^\pm = \pm \sqrt{2t^2 - 2t^2} = 0
\end{aligned}$$



2. If  $\epsilon \neq 0$

$$\text{At } k_x = \pi/a' = \pi/2a \Rightarrow \varepsilon_k^\pm = \pm \sqrt{2t^2 + 2\epsilon^2 - 2t^2 + 2\epsilon^2} = \pm 2\epsilon$$



(3) Peierls instability

The ground state energy for the lattice distortion is

$$\begin{aligned}
 \varepsilon &= -2 \int_0^{\pi/2a} \sqrt{2t^2 + 2\epsilon^2 + 2(t^2 - \epsilon^2) \cos 2k_x a} dk \\
 &= -2 \int_0^{\pi/2a} \sqrt{4t^2 \cos^2 k_x a + 4\epsilon^2 \sin^2 k_x a} dk \\
 &= -2 \int_0^{\pi/2a} \sqrt{2t^2 + 2\epsilon^2 + 2(t^2 - \epsilon^2)(1 - 2 \sin^2 k_x a)} dk \\
 &= -2 \int_0^{\pi/2a} \sqrt{4t^2 - 4(t^2 - \epsilon^2) \sin^2 k_x a} dk \\
 &= -4t \int_0^{\pi/2a} \sqrt{1 - \left(1 - \frac{\epsilon^2}{4t^2}\right) \sin^2 k_x a} dk \\
 &\approx -\frac{4t}{a} \left(1 - \frac{z}{4} \ln z\right) \text{ for } z \rightarrow 0
 \end{aligned}$$

where  $z = \epsilon^2 / 4t^2$

OS:

$$\int_0^{\pi/2a} \sqrt{1 - (1-z) \sin^2 ka} dk \approx 1 - \frac{z}{4} \ln z \text{ for } z \rightarrow 0$$

The ground state energy for free electrons is

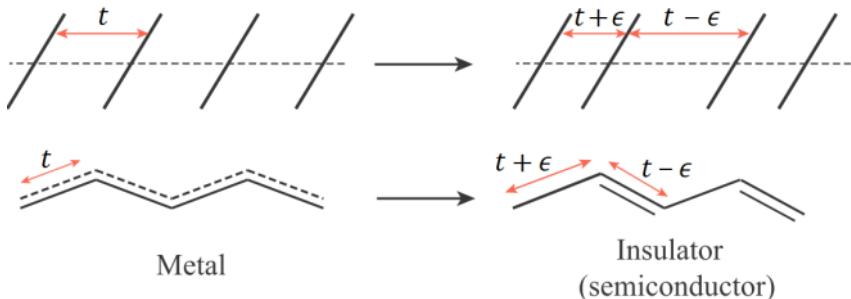
$$\begin{aligned}
 \varepsilon^0 &= -4t \int_0^{\pi/2a} \cos k_x a dk = -\frac{4t}{a} \\
 \varepsilon^0 - \varepsilon &= -\frac{z}{4} \ln z > 0 \text{ for } 0 < z < 1
 \end{aligned}$$

The lattice deformation (dimerization) has an energy that is lower by a logarithmic factor. The elastic energy gains lead to a lattice with short and long distances between neighboring atoms, so that the bonding between atoms alternates on going along the chain.

⇒ Peierls' theorem: a one-dimensional equally spaced chain with one electron per ion is unstable.

## -TRANS-POLYACETYLENE-

### (1) Trans-polyacetylene



## Two nearest-neighbors of an A-sublattice atom

$$\vec{\delta}_1 = \frac{a}{2} (1, \sqrt{3}), \quad \vec{\delta}_2 = \frac{a}{2} (-1, \sqrt{3})$$

The Hamiltonian is

$$\begin{aligned}
\mathcal{H} &= -(t + \epsilon) \sum_i a_i^\dagger b_i - (t - \epsilon) \sum_i a_i^\dagger b_{i+1} \\
&= -(t + \epsilon) \sum_i \frac{1}{N} \sum_{kk'} a_k^\dagger b_{k'} e^{-i\vec{k}\cdot\vec{R}_i} e^{i\vec{k}'\cdot(\vec{R}_i + \vec{a})} \\
&\quad - (t - \epsilon) \sum_i \frac{1}{N} \sum_{kk'} a_k^\dagger b_{k'} e^{-i\vec{k}\cdot\vec{R}_i} e^{i\vec{k}'\cdot(\vec{R}_i + \vec{a})} \\
&= -(t + \epsilon) \sum_k a_k^\dagger b_k e^{i\vec{k}\cdot\vec{a}} - (t - \epsilon) \sum_k a_k^\dagger b_k e^{i\vec{k}\cdot\vec{a}} \\
&= \sum_k \psi_k^\dagger \begin{pmatrix} 0 & h_k \\ h_k^* & 0 \end{pmatrix} \psi_k
\end{aligned}$$

where

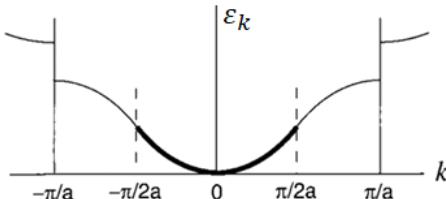
$$h_k = - \left\{ (t + \epsilon) e^{i \vec{k} \cdot \vec{a}} + (t - \epsilon) e^{i \vec{k} \cdot \vec{a}} \right\}$$

$$= - \left\{ (t + \epsilon) e^{-i(k_x a/2 - \sqrt{3} k_y a/2)} + (t - \epsilon) e^{i(k_x a/2 + \sqrt{3} k_y a/2)} \right\}$$

Energy band:

$$\begin{aligned}\varepsilon_k^{\pm} &= \pm\sqrt{h_k^* h_k} \\ &= \pm\sqrt{2t^2 + 2\epsilon^2 + (t^2 - \epsilon^2)(e^{-ik_x a} + e^{ik_x a})} \\ &= \pm\sqrt{2t^2 + 2\epsilon^2 + 2(t^2 - \epsilon^2) \cos k_x a}\end{aligned}$$

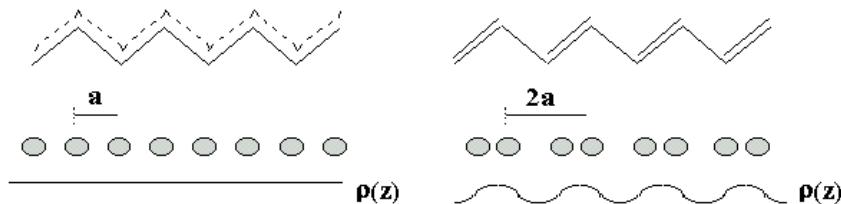
(2) For  $\epsilon = 0$



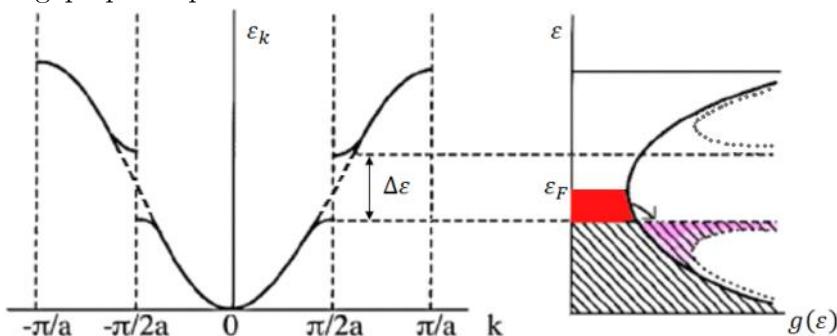
Fermi wave vector  $k_F = \pi/2a$ . The polyacetylene is a metal.

(3) For  $\epsilon \neq 0$

The lattice is dimerized and the effective unit-cell dimension is  $2a$ .



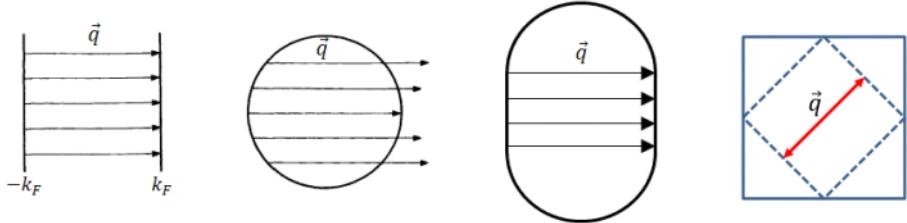
A gap opens up in the band at the Fermi level.



(4) A spatially periodic CDW is formed by the Fermi surface nesting  $q = 2k_F$ .

1. Fermi surface nesting

There are two parallel pieces of a Fermi surface, such that a single  $q$ -vector can connect many points.



1D: nesting

2D: no nesting

2D: partial nesting

2D: nesting

1D metal: Perfect nesting because the Fermi surface consists of two points at  $k_x = \pm k_F$ .

2D metal: NO good nesting because the Fermi surface is a circle. However, systems with stronger interactions (or quasi 1D bands) can have Fermi surface nesting.

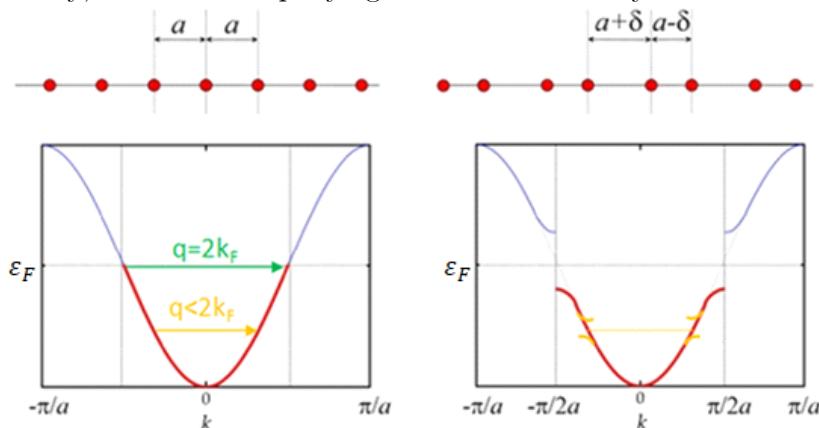
2D square lattice: Perfect nesting with  $\vec{q} = (\pi, \pi)/a$  at half filling.

## 2. Charge density wave driven by nesting

### OS:

As a disclaimer, not all charge density waves are driven by nesting, and not all Fermi surface topologies with a good nesting condition result in a CDW instability.

A charge density wave (CDW) is a periodic modulation of charge density, and an accompanying distortion of the crystal lattice.



The electrons near  $\epsilon_F$  can lower their energy and open up a gap at wavevector  $\pm 2\pi/a$  (corresponding to the Fermi surface nesting).

### OS:

This won't work for a wavevector connecting two states deep in the Fermi sea (orange) because the opening of a gap will raise the energy of electrons above the gap by an equal

amount that electrons below the gap lower their energy.  
A 1D metal is always unstable to the Peierls distortion and  
introduces a new periodicity  $q = 2k_F$  (CDW).

## 7-5 Electronic Band Structure

Tuesday, December 20, 2011 8:30 PM

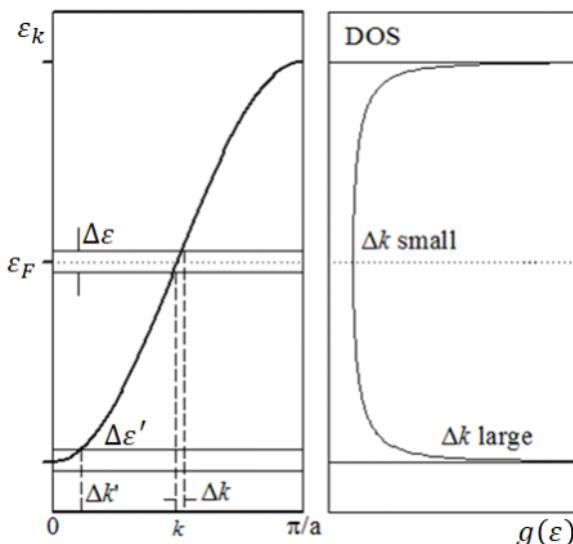
### A. CURVE OF ENERGY BAND

- (1) Inverse slope of bands

Density of states is proportional to the inverse slope of the band:

Steep bands  $\Rightarrow$  small DOS

Flat bands  $\Rightarrow$  large DOS



$g(\varepsilon_F)$  determines properties:

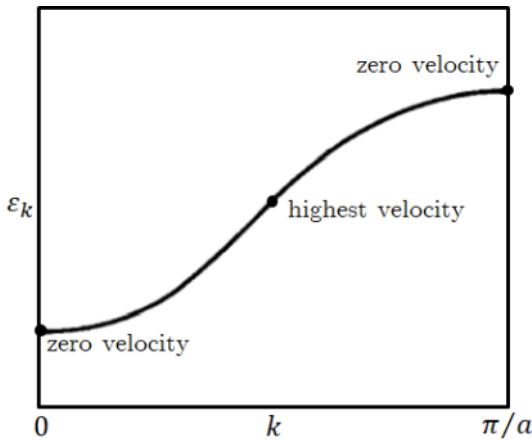
$g(\varepsilon_F) = 0$ : always nonmetallic

$g(\varepsilon_F) > 0$ : often metallic

- (2) Slope of bands

The mean velocity of an electron described by energy  $\varepsilon_k$  and wave vector  $k$

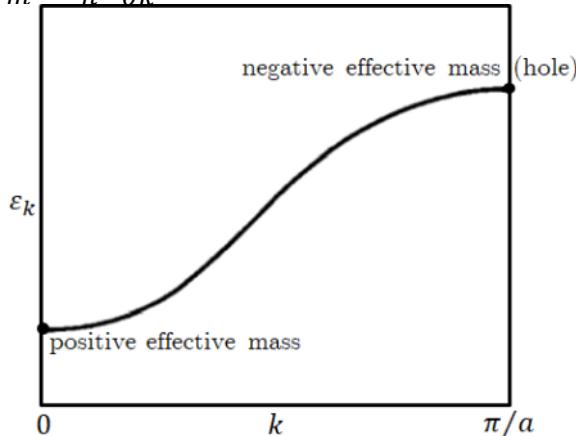
$$v = \frac{1}{\hbar} \frac{\partial \varepsilon_k}{\partial k}$$



### (3) Curvature of bands

The effective mass of a charge carrier near a band minimum or maximum is inversely proportional to the curvature of the band:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_k}{\partial k^2}$$



Parabolic approximation near minimum or maximum:

$$\begin{aligned}\varepsilon_k &= \frac{\hbar^2 k^2}{2m^*} \\ \frac{\partial^2 \varepsilon_k}{\partial k^2} &= \frac{\hbar^2}{m^*}\end{aligned}$$

## B. SYMMETRY OF ENERGY BAND

### (1) Point-group symmetry: rotation with respect to axes and reflection

across lines

Let  $\hat{\mathcal{S}}$  be the operator for a point-group symmetry operation ( $\hat{\mathcal{S}}^T = \hat{\mathcal{S}}^{-1}$ )

$$\vec{r}' = \hat{\mathcal{S}}\vec{r} \Rightarrow V(\hat{\mathcal{S}}\vec{r}) = V(\vec{r})$$

$$\hat{\mathcal{H}}_{\mathcal{S}r} = -\frac{\hbar^2 \nabla_{\mathcal{S}r}^2}{2m} + V(\hat{\mathcal{S}}\vec{r}) = -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) = \hat{\mathcal{H}}$$

Suppose one has solved the Schrödinger equation and obtained the Bloch state  $\psi_k(\vec{r})$  with energy  $\varepsilon_k$

$$\hat{\mathcal{H}}\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r})$$

Replace  $\vec{r}$  by  $\hat{\mathcal{S}}\vec{r}$

$$\hat{\mathcal{H}}_{\mathcal{S}r}\psi_k(\hat{\mathcal{S}}\vec{r}) = \varepsilon_k\psi_k(\hat{\mathcal{S}}\vec{r}) \Rightarrow \hat{\mathcal{H}}\psi_k(\hat{\mathcal{S}}\vec{r}) = \varepsilon_k\psi_k(\hat{\mathcal{S}}\vec{r})$$

Thus  $\psi_k(\hat{\mathcal{S}}\vec{r})$  is also a Bloch state with the same energy as  $\psi_k(\vec{r})$

From the Bloch theorem

$$\begin{aligned}\psi_k\left(\hat{\mathcal{S}}\left(\vec{r} + \vec{R}\right)\right) &= \psi_k\left(\hat{\mathcal{S}}\vec{r} + \mathcal{S}\vec{R}\right) \\ &= \psi_k(\hat{\mathcal{S}}\vec{r})e^{i\vec{k}\cdot\hat{\mathcal{S}}\vec{R}} \\ &= \psi_k(\hat{\mathcal{S}}\vec{r})e^{i\hat{\mathcal{S}}^{-1}\vec{k}\cdot\vec{R}} \\ &= \psi_{\mathcal{S}^{-1}k}(\vec{r})e^{i\hat{\mathcal{S}}^{-1}\vec{k}\cdot\vec{R}}\end{aligned}$$

$$\Rightarrow \psi_k(\hat{\mathcal{S}}\vec{r}) = \psi_{\mathcal{S}^{-1}k}(\vec{r})$$

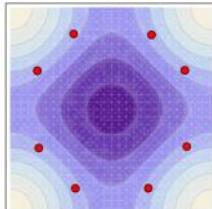
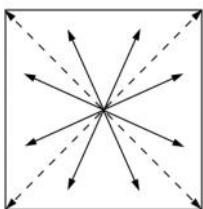
The energy of  $\psi_{\mathcal{S}^{-1}k}(\vec{r})$  is  $\varepsilon_k$ .

Therefore:

$$\varepsilon_{\mathcal{S}^{-1}k} = \varepsilon_k \Rightarrow \varepsilon_{\mathcal{S}k} = \varepsilon_k$$

**NOTE:**

1. If  $\mathcal{S}$  is a symmetry of the potential such that in real-space  $V(\hat{\mathcal{S}}\vec{r}) = V(\vec{r})$ , then the energy bands also enjoy the symmetry of potential such that in  $k$ -space:  $\varepsilon_{\mathcal{S}k} = \varepsilon_k$ .
2. Degeneracies in the energy bands can therefore arise from crystal point-group symmetries.



(2) Inversion symmetry

$$V(-\vec{r}) = V(\vec{r})$$

$$\hat{\mathcal{H}}_{-r} = -\frac{\hbar^2 \nabla^2}{2m} + V(-\vec{r}) = -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) = \hat{\mathcal{H}}$$

Suppose one has solved the Schrodinger equation and obtained the Bloch state  $\psi_k(\vec{r})$  with energy  $\varepsilon_k$

$$\hat{\mathcal{H}}\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r})$$

Replace  $\vec{r}$  by  $-\vec{r}$

$$\hat{\mathcal{H}}_{-r}\psi_k(-\vec{r}) = \varepsilon_k\psi_k(-\vec{r}) \Rightarrow \hat{\mathcal{H}}\psi_k(-\vec{r}) = \varepsilon_k\psi_k(-\vec{r})$$

We found a Bloch wavefunction  $\psi_k(-\vec{r})$  with the same energy as  $\psi_k(\vec{r})$

From the Bloch theorem

$$\begin{aligned} \psi_k\left(-(\vec{r} + \vec{R})\right) &= \psi_k(-\vec{r})e^{i\vec{k}\cdot(-\vec{R})} = \psi_k(-\vec{r})e^{i(-\vec{k})\cdot\vec{R}} = \psi_{-k}(\vec{r})e^{i(-\vec{k})\cdot\vec{R}} \\ \Rightarrow \psi_k(-\vec{r}) &= \psi_{-k}(\vec{r}) \\ \Rightarrow \varepsilon_{-k} &= \varepsilon_k \end{aligned}$$

### (3) Time-reversal symmetry

Suppose one has solved the time dependent Schrodinger equation and obtained the Bloch state  $\Psi_k(\vec{r}, t)$  with energy  $\varepsilon_k$

$$\hat{\mathcal{H}}\Psi_k(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi_k(\vec{r}, t)$$

$$\text{Let } \Psi_k(\vec{r}, t) = \psi_k(\vec{r})e^{iE_k t/\hbar}$$

$$\Rightarrow \hat{\mathcal{H}}\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r})$$

$$\Rightarrow \hat{\mathcal{H}}\psi_k^*(\vec{r}) = \varepsilon_k\psi_k^*(\vec{r})$$

We found a Bloch wavefunction  $\psi_k^*(\vec{r})$  with the same energy as  $\psi_k(\vec{r})$

Replace  $t$  by  $-t$

$$\hat{\mathcal{H}}\Psi_k(\vec{r}, -t) = -i\hbar \frac{\partial}{\partial t} \Psi_k(\vec{r}, -t) \Rightarrow \hat{\mathcal{H}}\Psi_k^*(\vec{r}, -t) = i\hbar \frac{\partial}{\partial t} \Psi_k^*(\vec{r}, -t)$$

This means that  $\Psi_k^*(\vec{r}, -t)$  is the time-reversal state corresponding to the state  $\Psi_k(\vec{r}, t)$ .

$$\Psi_k^*(\vec{r}, t) = \psi_k^*(\vec{r})e^{-i\varepsilon_k t/\hbar}$$

$\Rightarrow$  The function  $\psi_k^*(\vec{r})$  is the time-reversal Bloch state corresponding to  $\psi_k(\vec{r})$  with the same energy as  $\psi_k(\vec{r})$ .

From Bloch theorem

$$\begin{aligned} \psi_k^*(\vec{r} + \vec{R}) &= [\psi_k(\vec{r})e^{i\vec{k}\cdot\vec{R}}]^* = \psi_k^*(\vec{r})e^{i(-\vec{k})\cdot\vec{R}} = \psi_{-k}(\vec{r})e^{i(-\vec{k})\cdot\vec{R}} \\ \Rightarrow \psi_{-k}(\vec{r}) &= \psi_k^*(\vec{r}) \\ \Rightarrow \varepsilon_{-k} &= \varepsilon_k \end{aligned}$$

Kramer's theorem (Kramer's degeneracy 1930): if time-reversal symmetry is not broken, all eigenstates are at least doubly degenerate.

## C. SPIN-ORBIT INTERACTION AND SYMMETRY

- (1) Bloch states with spins:

The Bloch function can be written generally as a superposition of up and down spin states,

$$\psi_{k\chi}(\vec{r}) = \begin{pmatrix} \alpha_k(\vec{r}) \\ \beta_k(\vec{r}) \end{pmatrix} = \alpha_k(\vec{r})|\uparrow\rangle + \beta_k(\vec{r})|\downarrow\rangle$$

Lattice translation symmetry:

$$\psi_{k\chi}(\vec{r} + \vec{R}) = \begin{pmatrix} \alpha_k(\vec{r} + \vec{R}) \\ \beta_k(\vec{r} + \vec{R}) \end{pmatrix} = \begin{pmatrix} \alpha_k(\vec{r})e^{i\vec{k}\cdot\vec{R}} \\ \beta_k(\vec{r})e^{i\vec{k}\cdot\vec{R}} \end{pmatrix} = \psi_{k\chi}(\vec{r})e^{i\vec{k}\cdot\vec{R}}$$

- (2) Spin-orbit interaction:

An electron moving in an electric field sees an effective magnetic field

$$\vec{B}_{\text{eff}} = \frac{\vec{E} \times \vec{P}}{2mc^2}$$

The magnetic moment of an electron is given by

$$\vec{\mu} = -2 \frac{\mu_B}{\hbar} \vec{S}$$

The interaction between the electron spin and the effective magnetic field adds a new term to the Hamiltonian,

$$\hat{\mathcal{H}}_{\text{SO}} = -\hat{\mu} \cdot \vec{B}_{\text{eff}}, \quad \hat{\mu} = -\mu_B \hat{\sigma}$$

where the Pauli matrices are

$$\begin{aligned} \sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, & \sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, & \sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ \hat{\mathcal{H}}_{\text{SO}} &= \mu_B \hat{\sigma} \cdot \frac{\vec{E} \times \hat{\vec{p}}}{2mc^2} = \frac{e\hbar}{2m} \hat{\sigma} \cdot \left[ \frac{1}{2emc^2} \nabla V(\vec{r}) \times \hat{\vec{p}} \right] \\ &= \frac{\hbar}{4m^2 c^2} \hat{\sigma} \cdot [\nabla V(\vec{r}) \times \hat{\vec{p}}] \\ \hat{\mathcal{H}} &= \frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) + \frac{\hbar}{4m^2 c^2} \hat{\sigma} \cdot [\nabla V(\vec{r}) \times \hat{\vec{p}}] \\ \hat{\mathcal{H}} \psi_{k\chi}(\vec{r}) &= \varepsilon_{k\chi} \psi_{k\chi}(\vec{r}) \end{aligned}$$

In the presence of spin-orbit coupling, spin is not a good quantum number

$$[\hat{\mathcal{H}}, \hat{\sigma}] \neq 0$$

(3) Point-group symmetry

Let  $\mathcal{S}$  be the operator for a point-group symmetry operation ( $\mathcal{S}^T = \mathcal{S}^{-1}$ )

$$V(\mathcal{S}\vec{r}) = V(\vec{r})$$

The Schrödinger equation

$$\begin{aligned} \widehat{\mathcal{H}}\psi_{k\chi}(\vec{r}) &= \varepsilon_{k\chi}\psi_{k\chi}(\vec{r}) \\ \left\{ -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla V(\vec{r})\times\nabla] \right\} \psi_{k\chi}(\vec{r}) &= \varepsilon_{k\chi}\psi_{k\chi}(\vec{r}) \end{aligned}$$

Replace  $\vec{r}$  by  $\mathcal{S}\vec{r}$

$$\begin{aligned} \widehat{\mathcal{H}}_{\mathcal{S}r}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) &= \varepsilon_{k\chi}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \\ \left\{ -\frac{\hbar^2\nabla_{\mathcal{S}r}^2}{2m} + V(\hat{\mathcal{S}}\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla_{\mathcal{S}r}V(\hat{\mathcal{S}}\vec{r})\times\nabla_{\mathcal{S}r}] \right\} \psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) &= \varepsilon_{k\chi}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \\ \left\{ -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot\hat{\mathcal{S}}[\nabla V(\vec{r})\times\nabla] \right\} \psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) &= \varepsilon_{k\chi}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \end{aligned}$$

Define a unitary spin rotation operator  $\mathcal{R}$  that operates in the Hilbert space of spins and rotates spin states in the sense of the operator  $\mathcal{S}$ .

Consider a spinor pointing in the  $\hat{n}$  direction

$$\begin{aligned} \vec{\sigma}\cdot\hat{n} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} &= \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \\ \Rightarrow (\vec{\sigma}\cdot\hat{n})\mathcal{R}^{-1}\mathcal{R} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} &= \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \\ \Rightarrow \mathcal{R}(\vec{\sigma}\cdot\hat{n})\mathcal{R}^{-1}\mathcal{R} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} &= \mathcal{R} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \\ \Rightarrow (\vec{\sigma}\cdot\mathcal{S}\hat{n})\mathcal{R} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} &= \mathcal{R} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \\ \Rightarrow \mathcal{R}(\vec{\sigma}\cdot\hat{n})\mathcal{R}^{-1} &= \vec{\sigma}\cdot\mathcal{S}\hat{n} \quad \text{or} \quad \mathcal{R}^{-1}(\vec{\sigma}\cdot\mathcal{S}\hat{n})\mathcal{R} = \vec{\sigma}\cdot\hat{n} \end{aligned}$$

Introduce spin rotation operator  $\mathcal{R}$  corresponding to the rotation generated by the matrix  $\mathcal{S}$ .

$$\begin{aligned} \mathcal{R}^{-1} \left\{ -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot\hat{\mathcal{S}}[\nabla V(\vec{r})\times\nabla] \right\} \mathcal{R}\mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \\ = \varepsilon_{k\chi}\mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \\ \left\{ -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla V(\vec{r})\times\nabla] \right\} \mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \\ = \varepsilon_{k\chi}\mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r}) \end{aligned}$$

The new state  $\mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r})$  has the same energy as  $\psi_{k\chi}(\vec{r})$

From Bloch theorem

$$\begin{aligned}\mathcal{R}^{-1}\psi_{k\chi}\left(\hat{\mathcal{S}}\left(\vec{r} + \vec{R}\right)\right) &= \mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r})e^{i\vec{k}\cdot\vec{S}\vec{R}} \\ &= \mathcal{R}^{-1}\psi_{k\chi}(\hat{\mathcal{S}}\vec{r})e^{i\mathcal{S}^{-1}\vec{k}\cdot\vec{R}} \\ &= \mathcal{R}^{-1}\psi_{\mathcal{S}^{-1}k\chi}(\vec{r})e^{i\mathcal{S}^{-1}\vec{k}\cdot\vec{R}}\end{aligned}$$

$$\Rightarrow \varepsilon_{\mathcal{S}^{-1}k\chi} = \varepsilon_{k\chi}$$

(4) Inversion symmetry

$$V(-\vec{r}) = V(\vec{r})$$

The Schrödinger equation

$$\left\{-\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla V(\vec{r})\times\nabla]\right\}\psi_{k\chi}(\vec{r}) = \varepsilon_{k\chi}\psi_{k\chi}(\vec{r})$$

Replace  $\vec{r}$  by  $-\vec{r}$

$$\begin{aligned}\left\{-\frac{\hbar^2\nabla_{-\vec{r}}^2}{2m} + V(-\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla_{-\vec{r}}V(-\vec{r})\times\nabla_{-\vec{r}}]\right\}\psi_{k\chi}(-\vec{r}) \\ = \varepsilon_{k\chi}\psi_{k\chi}(-\vec{r}) \\ \left\{-\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla V(\vec{r})\times\nabla]\right\}\psi_{k\chi}(-\vec{r}) = \varepsilon_{k\chi}\psi_{k\chi}(-\vec{r})\end{aligned}$$

The new state  $\psi_{k\chi}(-\vec{r})$  has the same energy as  $\psi_{k\chi}(\vec{r})$

From Bloch theorem

$$\psi_{k\chi}\left(-\left(\vec{r} + \vec{R}\right)\right) = \psi_{k\chi}(-\vec{r})e^{i(-\vec{k})\cdot\vec{R}} = \psi_{-k\chi}(\vec{r})e^{i(-\vec{k})\cdot\vec{R}}$$

Since the total angular momentum operators are invariant under spatial inversion

$$\hat{J}_z\psi_{k\chi}(\vec{r}) = \chi\psi_{k\chi}(\vec{r}) \Rightarrow \hat{J}_z\psi_{k\chi}(-\vec{r}) = \chi\psi_{k\chi}(-\vec{r})$$

So  $\psi_{k\chi}(-\vec{r})$  has the same angular momentum as  $\psi_{k\chi}(\vec{r})$

Therefore, we can write

$$\psi_{k\chi}(-\vec{r}) = \psi_{-k\chi}(\vec{r})$$

$$\Rightarrow \varepsilon_{-k\chi} = \varepsilon_{k\chi}$$

(5) Time-reversal symmetry

The time-dependent Schrodinger equation

$$\left\{-\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot[\nabla V(\vec{r})\times\nabla]\right\}\Psi_{k\chi}(\vec{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi_{k\chi}(\vec{r}, t)$$

Solution:

$$\Psi_{k\chi}(\vec{r}, t) = \psi_{k\chi}(\vec{r}) e^{iEt/\hbar}$$

Replace  $t$  by  $-t$

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) - i \frac{\hbar^2}{4m^2 c^2} \vec{\sigma} \cdot [\nabla V(\vec{r}) \times \nabla] \right\} \Psi_{k\chi}(\vec{r}, -t)$$

$$= -i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}(\vec{r}, -t)$$

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) + i \frac{\hbar^2}{4m^2 c^2} \vec{\sigma}^* \cdot [\nabla V(\vec{r}) \times \nabla] \right\} \Psi_{k\chi}^*(\vec{r}, -t)$$

$$= i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}^*(\vec{r}, -t)$$

Try a transformation with the unitary matrix  $-i\sigma_y$  with the equation

$$(-i\sigma_y) \left\{ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) + i \frac{\hbar^2}{4m^2 c^2} \vec{\sigma}^* \cdot [\nabla V(\vec{r}) \times \nabla] \right\} (-i\sigma_y)$$

$$\times (-i\sigma_y) \begin{pmatrix} \alpha_k^*(\vec{r}, -t) \\ \beta_k^*(\vec{r}, -t) \end{pmatrix} = i\hbar \frac{\partial}{\partial t} (-i\sigma_y) \begin{pmatrix} \alpha_k^*(\vec{r}, -t) \\ \beta_k^*(\vec{r}, -t) \end{pmatrix}$$

where

$$\vec{\sigma} = \sigma_x \hat{x} + \sigma_y \hat{y} + \sigma_z \hat{z}$$

$$\vec{\sigma}^* = \sigma_x \hat{x} - \sigma_y \hat{y} + \sigma_z \hat{z} \neq \vec{\sigma}$$

$$(-i\sigma_y) \vec{\sigma}^* (-i\sigma_y) = \sigma_y \sigma_x \sigma_y \hat{x} - \sigma_y \sigma_y \sigma_y \hat{y} + \sigma_y \sigma_z \sigma_y \hat{z}$$

$$= -\sigma_x \hat{x} + \sigma_y \hat{y} - \sigma_z \hat{z}$$

$$= -\vec{\sigma}$$

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) - i \frac{\hbar^2}{4m^2 c^2} \vec{\sigma} \cdot [\nabla V(\vec{r}) \times \nabla] \right\} \begin{pmatrix} -\beta_k^*(\vec{r}, -t) \\ \alpha_k^*(\vec{r}, -t) \end{pmatrix}$$

$$= i\hbar \frac{\partial}{\partial t} \begin{pmatrix} -\beta_k^*(\vec{r}, -t) \\ \alpha_k^*(\vec{r}, -t) \end{pmatrix}$$

where

$$(-i\sigma_y) \begin{pmatrix} \alpha_k^*(\vec{r}, -t) \\ \beta_k^*(\vec{r}, -t) \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha_k^*(\vec{r}, -t) \\ \beta_k^*(\vec{r}, -t) \end{pmatrix} = \begin{pmatrix} -\beta_k^*(\vec{r}, -t) \\ \alpha_k^*(\vec{r}, -t) \end{pmatrix}$$

The time-reversed Bloch state has the same energy as the original state.

$$\begin{pmatrix} -\beta_k^*(\vec{r}, -t) \\ \alpha_k^*(\vec{r}, -t) \end{pmatrix} = \begin{pmatrix} -\beta_k^*(\vec{r}) e^{-iEt/\hbar} \\ \alpha_k^*(\vec{r}) e^{-iEt/\hbar} \end{pmatrix} = \begin{pmatrix} -\beta_k^*(\vec{r}) \\ \alpha_k^*(\vec{r}) \end{pmatrix} e^{-iEt/\hbar}$$

From Bloch theorem

$$\begin{pmatrix} -\beta_k^*(\vec{r} + \vec{R}) \\ \alpha_k^*(\vec{r} + \vec{R}) \end{pmatrix} = e^{-i\vec{k}\cdot\vec{R}} \begin{pmatrix} -\beta_k^*(\vec{r}) \\ \alpha_k^*(\vec{r}) \end{pmatrix} = \psi_{-k\chi}(\vec{r}) e^{i(-\vec{k})\cdot\vec{R}}$$

So the new solution is a Bloch state with wavevector  $-\vec{k}$

$$\psi_{-k\chi}(\vec{r}) = \begin{pmatrix} -\beta_k^*(\vec{r}) \\ \alpha_k^*(\vec{r}) \end{pmatrix} = (-i\sigma_y) \psi_{k\chi}^*(\vec{r})$$

The total angular momentum operator

$$\hat{J}_z \begin{pmatrix} -\beta_k^*(\vec{r}) \\ \alpha_k^*(\vec{r}) \end{pmatrix} = \hat{J}_z (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) = -\chi (-i\sigma_y) \psi_{k\chi}^*(\vec{r})$$

**PROOF:**

$$\begin{aligned} \hat{J}_z \psi_{k\chi}(\vec{r}) &= \chi \psi_{k\chi}(\vec{r}) \\ \Rightarrow \hat{J}_z^* \psi_{k\chi}^*(\vec{r}) &= \chi \psi_{k\chi}^*(\vec{r}) \\ \Rightarrow (-i\sigma_y)(-\hat{L}_z + \hat{S}_z)(i\sigma_y)(-i\sigma_y) \psi_{k\chi}^*(\vec{r}) &= \chi (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) \\ \Rightarrow (-\hat{L}_z - \hat{S}_z)(-i\sigma_y) \psi_{k\chi}^*(\vec{r}) &= \chi (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) \\ \Rightarrow -(\hat{L}_z + \hat{S}_z)(-i\sigma_y) \psi_{k\chi}^*(\vec{r}) &= \chi (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) \\ \Rightarrow (\hat{L}_z + \hat{S}_z)(-i\sigma_y) \psi_{k\chi}^*(\vec{r}) &= -\chi (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) \\ \Rightarrow \hat{J}_z (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) &= -\chi (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) \end{aligned}$$

■

The new solution is also an eigenfunction of  $\hat{J}_z$  with an eigenvalue  $-\chi$ . Therefore, the new solution is the Bloch state

$$\psi_{-k,-\chi}(\vec{r}) = (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) = \begin{pmatrix} -\beta_k^*(\vec{r}) \\ \alpha_k^*(\vec{r}) \end{pmatrix}$$

with the same energy as  $\psi_{k\chi}(\vec{r})$

**OS:**

$$\begin{aligned} \text{Time-reversal operator: } (-i\sigma_y) \hat{C} \psi_{k\chi}(\vec{r}) &= (-i\sigma_y) \psi_{k\chi}^*(\vec{r}) = \\ \psi_{-k,-\chi}(\vec{r}) & \\ \Rightarrow \varepsilon_{-k,-\chi} &= \varepsilon_{k\chi} \end{aligned}$$

## D. CRYSTAL SYMMETRY BROKEN

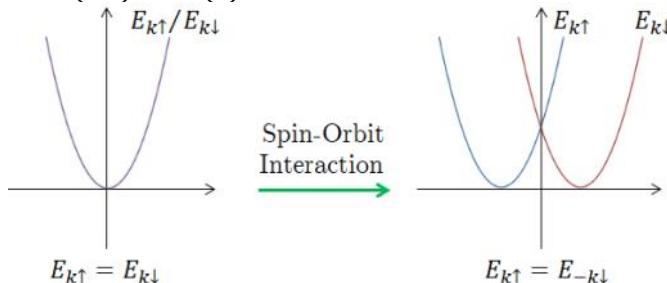
(1) Inversion symmetry broken

Rashba spin-orbital interaction breaks the inversion symmetry

$$\begin{aligned}
\nabla V(\vec{r}) &= -\frac{dV}{dz} \hat{z} \\
\widehat{\mathcal{H}}_0 &= \frac{\not{p}^2}{2m} + V(\vec{r}) \\
\widehat{\mathcal{H}}_{SO} &= \frac{\hbar}{4m^2c^2} \hat{\sigma} \cdot [\nabla V(\vec{r}) \times \vec{p}] \\
&= -\frac{\hbar}{4m^2c^2} \vec{\sigma} \cdot \left[ \frac{dV}{dz} \hat{z} \times \vec{p} \right] \\
&= -\frac{\hbar}{4m^2c^2} \frac{dV}{dz} \begin{vmatrix} \sigma_x & \sigma_y & \sigma_z \\ 0 & 0 & 1 \\ p_x & p_y & p_z \end{vmatrix} \\
&= \frac{\hbar}{4m^2c^2} \frac{dV}{dz} (\sigma_x p_y - \sigma_y p_x)_z \\
&= \frac{\alpha_R}{\hbar} (\vec{\sigma} \times \vec{p})_z
\end{aligned}$$

Replace  $\vec{r}$  by  $-\vec{r}$

$$\begin{aligned}
\Rightarrow \widehat{\mathcal{H}}_{SO}(-\vec{r}) &= -\widehat{\mathcal{H}}_{SO}(\vec{r}) \\
\Rightarrow \widehat{\mathcal{H}}(-\vec{r}) &\neq \widehat{\mathcal{H}}(\vec{r})
\end{aligned}$$



OS:

The Rashba effect, discovered in 1959 by a Soviet-American theoretical physicist Emmanuel Rashba.

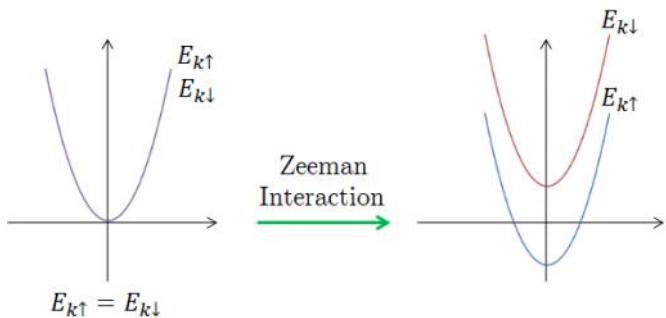
(2) Time-reversal symmetry broken

Magnetic field breaks the time-reversal symmetry

$$\begin{aligned}
\widehat{\mathcal{H}}_0 &= \frac{\left( \vec{p} + \frac{e}{c} \vec{A} \right)^2}{2m} + V(\vec{r}) \\
\left\{ \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 + V(\vec{r}) \right\} \Psi_{k\chi}(\vec{r}, t) &= i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}(\vec{r}, t)
\end{aligned}$$

Replace  $t$  by  $-t$

$$\begin{aligned} & \left\{ \frac{\left( -i\hbar\nabla + \frac{e}{c}\vec{A} \right)^2}{2m} + V(\vec{r}) \right\} \Psi_{k\chi}(\vec{r}, -t) = -i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}(\vec{r}, -t) \\ & \left\{ \frac{-\hbar^2 \nabla^2 - 2i\hbar \frac{e}{c} \nabla \cdot \vec{A} + \frac{e^2}{c^2} A^2}{2m} + V(\vec{r}) \right\} \Psi_{k\chi}(\vec{r}, -t) = -i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}(\vec{r}, -t) \\ & \left\{ \frac{-\hbar^2 \nabla^2 + 2i\hbar \frac{e}{c} \nabla \cdot \vec{A} + \frac{e^2}{c^2} A^2}{2m} + V(\vec{r}) \right\} \Psi_{k\chi}^*(\vec{r}, -t) = i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}^*(\vec{r}, -t) \\ & \left\{ \frac{\left( \vec{p} - \frac{e}{c}\vec{A} \right)^2}{2m} + V(\vec{r}) \right\} \Psi_{k\chi}^*(\vec{r}, -t) = i\hbar \frac{\partial}{\partial t} \Psi_{k\chi}^*(\vec{r}, -t) \\ & \Rightarrow \hat{\mathcal{H}}_0^*(\vec{r}) \neq \hat{\mathcal{H}}_0(\vec{r}) \end{aligned}$$



# 7-6 Metal & Insulator

Tuesday, December 20, 2011 8:30 PM

## A. METAL & INSULATOR

- (1) Quantum treatment of electric field  $\vec{E}_0$

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + V(\vec{r}) + e\vec{E}_0 \cdot \vec{r} \equiv \hat{\mathcal{H}}_0 + e\vec{E}_0 \cdot \vec{r}$$

where  $\hat{\mathcal{H}}_0\psi_k(\vec{r}) = \epsilon_k\psi_k(\vec{r})$

Assume the electric field is applied at time  $t = 0$

$$\psi_k(\vec{r}, 0) = \psi_k(\vec{r})$$

The time evolution is

$$\psi_k(\vec{r}, t) = e^{-i\mathcal{H}t/\hbar}\psi_k(\vec{r}, 0)$$

Since the term  $\vec{E}_0 \cdot \vec{r}$  breaks the invariance of the lattice translation, the effect of the translation operator is

$$\begin{aligned}\hat{T}_R\psi_k(\vec{r}, t) &= \hat{T}_R e^{-i\mathcal{H}t/\hbar}\psi_k(\vec{r}, 0) \\ &= \hat{T}_R e^{-i\mathcal{H}t/\hbar}\hat{T}_R^{-1}\hat{T}_R\psi_k(\vec{r}, 0) \\ &= e^{-i\hat{T}_R\mathcal{H}\hat{T}_R^{-1}t/\hbar}\hat{T}_R\psi_k(\vec{r}, 0) \\ &= e^{-i(\mathcal{H}+e\vec{E}_0 \cdot \vec{R})t/\hbar}\hat{T}_R\psi_k(\vec{r}, 0)\end{aligned}$$

and

$$\hat{T}_R\psi_k(\vec{r}, 0) = \hat{T}_R\psi_k(\vec{r}) = \psi_k(\vec{r})e^{i\vec{k} \cdot \vec{R}} = \psi_k(\vec{r}, 0)e^{i\vec{k} \cdot \vec{R}}$$

Therefore

$$\begin{aligned}\hat{T}_R(\vec{r}, t) &= e^{-i(\mathcal{H}+e\vec{E}_0 \cdot \vec{R})t/\hbar}\psi_k(\vec{r}, 0)e^{i\vec{k} \cdot \vec{R}} \\ &= e^{i(\vec{k}-e\vec{E}_0 t/\hbar) \cdot \vec{R}}e^{-i\mathcal{H}t/\hbar}\psi_k(\vec{r}, 0) \\ &= \psi_k(\vec{r}, t)e^{i(\vec{k}-e\vec{E}_0 t/\hbar) \cdot \vec{R}}\end{aligned}$$

Although  $\psi_k(\vec{r}, t)$  obeys Bloch's theorem with a time-dependent wave vector

$$\vec{k}(t) = \vec{k}(0) - \frac{e\vec{E}_0 t}{\hbar},$$

$\psi_k(\vec{r}, t)$  is not an eigenfunction of  $\mathcal{H}$ .

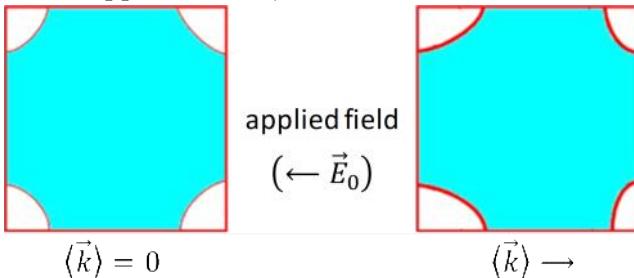
If the electric field is turned off at time  $t$ , without causing an interband transition (adiabatic approximation), at subsequent times the electron will be found in an eigenstate of  $\mathcal{H}_0$  corresponding to the wave vector

$\vec{k}(t)$ . Since the turned off time is arbitrarily, the time evolution as if the electron were continually visiting the states of  $\mathcal{H}_0$  with its wave vector varying in time is according to the equation of motion

$$\hbar \dot{\vec{k}}(t) = -e \vec{E}_0$$

## (2) Partial-filled band

When applied a field, the Fermi surface is shifted.



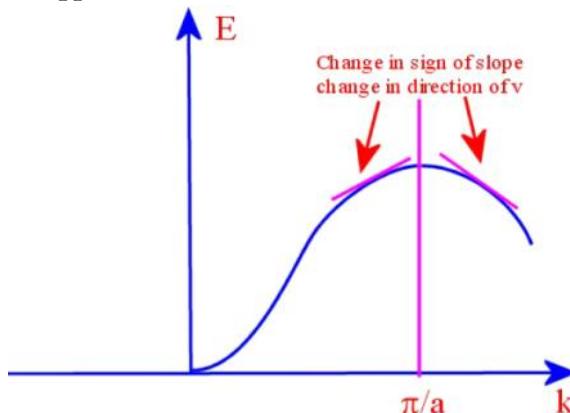
$$\text{group velocity } \vec{v} = \frac{d\omega}{d\vec{k}} = \frac{1}{\hbar} \frac{d\mathcal{E}_k}{d\vec{k}}$$

$$\vec{j} = -e \langle \vec{v} \rangle \neq 0$$

$\Rightarrow$  metal

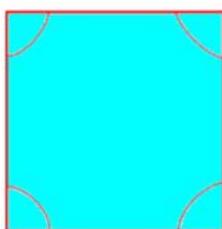
## (3) Filled band

Bragg reflection:

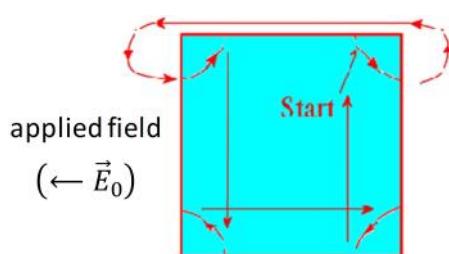


On crossing the zone boundary, the group velocity changes direction  $\rightarrow$  the electron is reflected.

When applied a field, electrons'  $k$ -values increased.



$$\langle \vec{k} \rangle = 0$$



$$\langle \vec{k} \rangle = 0$$

Electrons at the zone boundary are Bragg reflected back to the other side of the zone.

$$\vec{j} = -e\langle \vec{v} \rangle = 0$$

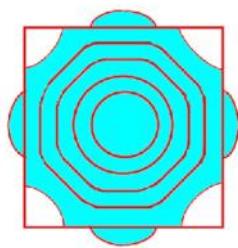
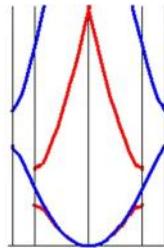
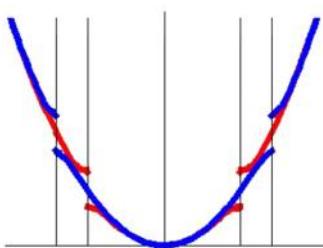
$\Rightarrow$  insulator

A filled band does not carry current (Peierls, 1929)

### EXAMPLES:

Divalent metal in two dimension: The area of  $k$ -space needed to accommodate all the electrons is equal to the area of the first Brillouin zone.

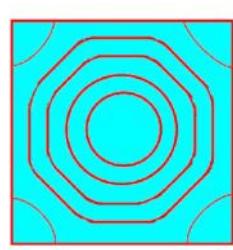
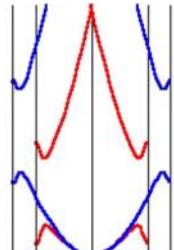
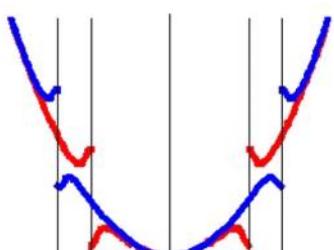
1. Small gap



The filled states are in both the first and second zones.

$\Rightarrow$  metal

2. Large gap



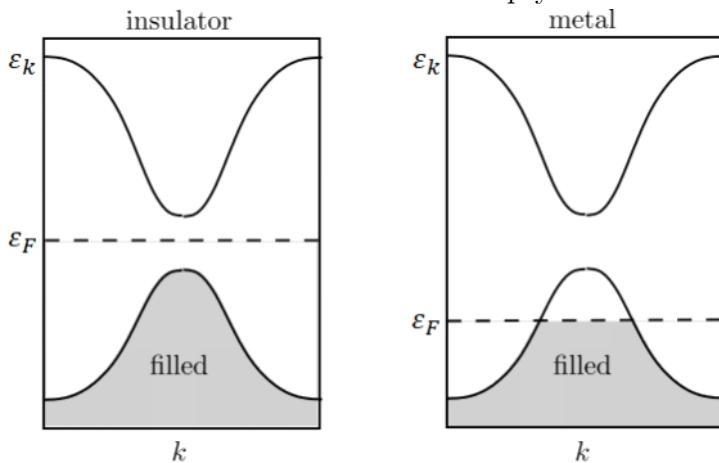
The whole of the first Brillouin zone are filled.

$\Rightarrow$  insulator

- (4) Difference between conductor and insulator (Wilson, 1931)

Metal: at least one band is partially occupied.

Insulator: all bands are either full or empty.

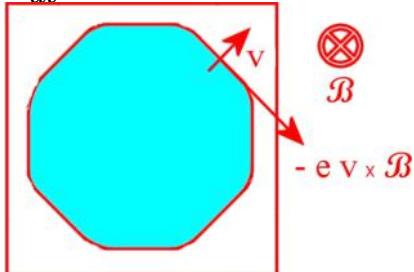


## B. METAL AND FERMI SURFACE

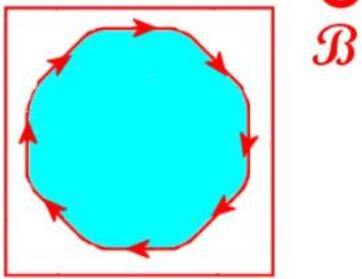
- (1) Apply a magnetic field  $\vec{B}$

The change in  $\vec{k}$  is perpendicular to both  $\vec{v}$  and  $\vec{B}$

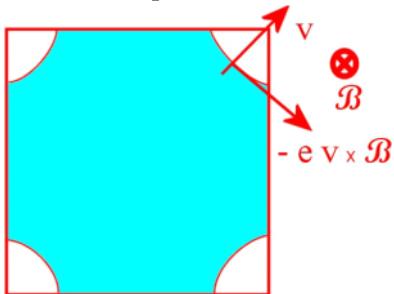
$$\hbar \frac{d\vec{k}}{dt} = -e\vec{v} \times \vec{B}$$



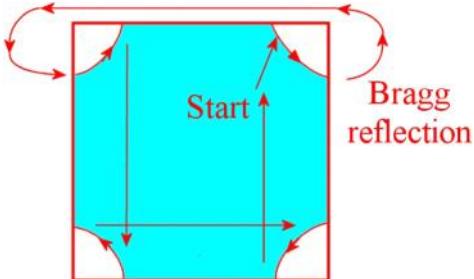
The electron stays on the constant energy surface



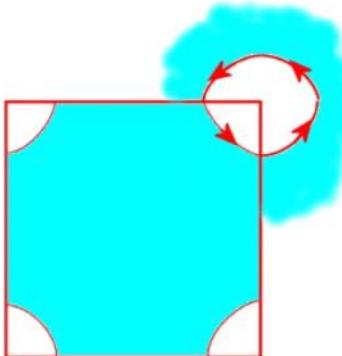
(2) Near the top of a band



The electrons are Bragg reflected at the edges of the Brillouin zone

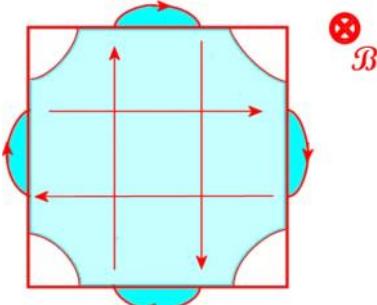


The electrons orbit, in k-space, the opposite way round occupied or unoccupied states.

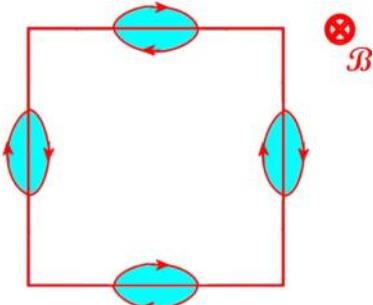


The behavior looks like that of an opposite charged particle - a hole.

(3) Electrons in the second zone



Using the periodic nature of the system and redrawing the Fermi surface



This is electron-like behavior.

## C. INSULATOR AND ENERGY GAP

- (1) Insulators exhibit an energy gap for single-electron excitations as a results of electron-ion or electron-electron interactions.
- (2) Trivial insulator:
  1. Insulators can be understood in terms of a single-electron theory:
    - (a) Band insulator (Bloch insulator): due to the interaction between electron and periodic potential of the ions.
    - (b) Peierls insulator: due to the interaction between electron and static lattice deformations, leading to a commensurate charge-density wave of the electrons.
    - (c) Anderson insulator: due to the interaction between electron and disorders, such as impurities and lattice imperfections.

2. Insulators arise from electron-electron interactions.

(a) Mott insulator: due to the strong correlation effects induced by large on-site Coulomb interactions.

(3) Topological insulator:

Insulator due to the interaction between electrons' spin and orbital.

# 8-1 Jellium Model

Tuesday, December 20, 2011 8:30 PM

## A. THE MANY-BODY HAMILTONIAN

- (1) The many-body Hamiltonian

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{kin}} + V_{\text{ee}} + V_{\text{ion}} + \hat{\mathcal{H}}_{\text{ii}}$$
$$\hat{\mathcal{H}}_{\text{kin}} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m}$$

$$V_{\text{ee}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$V_{\text{ion}} = - \sum_{i=1}^N \sum_{l=1}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_l}{|\vec{r}_i - \vec{R}_l|}$$

$$\begin{aligned} \hat{\mathcal{H}}_{\text{ii}} &= \sum_{I=1}^N \frac{\hat{p}_I^2}{2m} + \sum_{I=1}^{N-1} \sum_{J=I+1}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \\ &= \sum_{I=1}^N \frac{\hat{p}_I^2}{2m} + \frac{1}{2} \sum_{I=1}^{N-1} \sum_{J \neq I}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \end{aligned}$$

$$\text{where } \sum_{i < j} \equiv \sum_{i < j} \sum_j^N = \sum_{i=1}^{N-1} \sum_{j=i+1}^N = \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N$$

- (2) Born-Oppenheimer approximation: the time scale of the motion of electrons is much larger than the nuclei and thus the response time of the electrons to any change in the positions of the nuclei is considered immediate.

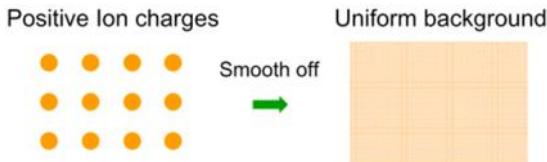
$$\hat{\mathcal{H}}_{\text{ii}} \approx V_{\text{ii}} = \frac{1}{2} \sum_{I=1}^{N-1} \sum_{J \neq I}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

$$\hat{\mathcal{H}} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + V_{\text{ee}} + V_{\text{ion}} + V_{\text{ii}}$$

## B. JELLIUM MODEL

## (1) Jellium model

The positive ions behave like a rigid jelly with uniform density of positive charge. Jellium is just a collection of electrons, into which ions are introduced as a spatially uniform background to maintain overall charge neutrality, i.e.



The jellium Hamiltonian can then be written as

$$\hat{\mathcal{H}} = \sum_{i=1}^N \left( \frac{\hat{p}_i^2}{2m} + v_{\text{ion}}(\vec{r}_i) \right) + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N v_{ee}(\vec{r}_i, \vec{r}_j)$$

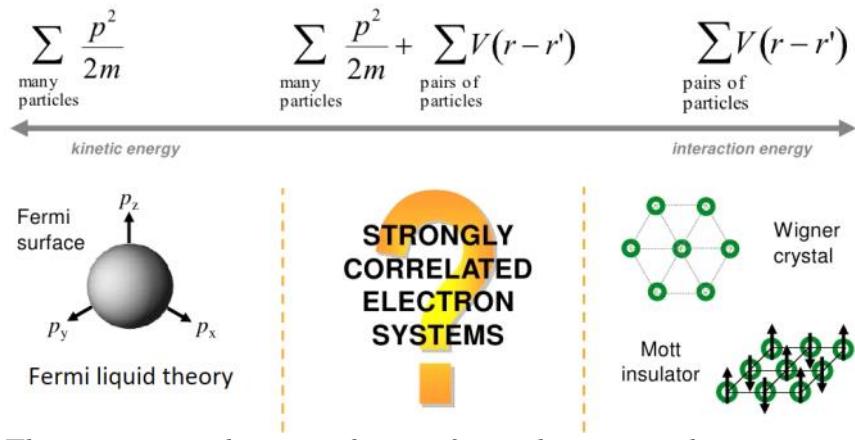
where

$$v_{\text{ion}}(\vec{r}_i) = - \sum_{I=1}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|}$$

$$v_{ee}(\vec{r}_i, \vec{r}_j) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Jellium model assumes interacting electrons in a smeared potential of ions (no lattice structure considered)

- (2) There are two competing forces: the Coulomb energy versus the kinetic energy.



The competition between the two forces determines the properties of

the material.

### C. CRITERION

#### (1) Bandwidth ( $W$ )

1. Wide bands:  $W > V$

The Coulomb interaction is well screened and the kinetic energy prevails. The system can be well described by the one-electron theory based on Bloch's theorem.

2. Narrow bands:  $W < V$

The Coulomb interaction tends to localize the electrons and the system is an insulator at half filling. The Mott insulating state is often found in the transition-metal oxides.

#### (2) Electron density ( $n$ )

The ratio between Coulomb energy and kinetic energy is

$$\frac{V_{ee}(r_s)}{\varepsilon_{\text{kin}}(r_s)} \propto \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_s} / \frac{\hbar^2}{mr_s^2} = \frac{r_s}{a_0}$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \text{ \AA}$$

$r_s$  is the average distance between electrons.

**PROOF:**

The kinetic energy per electron is [c.f.5-2-B]

$$\varepsilon_{\text{kin}} = \frac{E_{\text{kin}}}{N} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m}$$

The average volume occupied by one electron is

$$\frac{4\pi}{3} r_s^3 = \frac{\mathcal{V}}{N} = \frac{1}{n}$$

$$\Rightarrow k_F = (3\pi^2 n)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s}$$

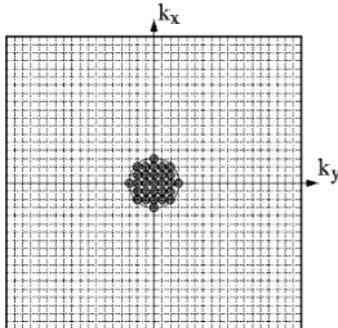
$$\Rightarrow \varepsilon_{\text{kin}} \propto \frac{\hbar^2}{mr_s^2}$$

1. High density limit

$r_s \ll a_0 \Rightarrow V_{ee} \ll \varepsilon_{\text{kin}} \Rightarrow$  weakly correlated system

In this regime, the free electron approximation (ignoring

interactions) is a good approximation.

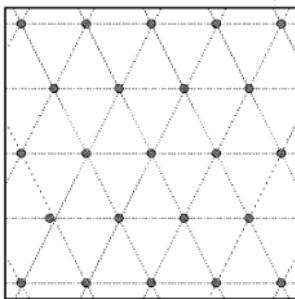


Electrons localized in  $k$ -space (Fermi liquid behavior)

## 2. Low density limit

$r_s \gg a_0 \Rightarrow V_{ee} \gg \varepsilon_{kin} \Rightarrow$  strongly correlated system

In this regime, electrons want to stay as far away from each other as possible to reduce the interaction energy. In 2D, they form a close pack structure (a triangular lattice), called Wigner crystal.



Electrons localized in real space (Wigner crystal)

# 8-2 Hatree-Fock Approximation

Tuesday, December 20, 2011 8:30 PM

## A. THE RITZ VARIATIONAL PRINCIPLE

- (1) A function  $\psi$  for which  $\langle \hat{\mathcal{H}} \rangle$  is stationary, i.e.,  $\delta \langle \hat{\mathcal{H}} \rangle = 0$ , is the eigenfunction of the energy.

PROOF:

$$\langle \hat{\mathcal{H}} \rangle = \int \psi^* \hat{\mathcal{H}} \psi d^3r$$

Use the Lagrange multiplier  $\lambda$

$$\begin{aligned} & \delta \left( \int \psi^* \hat{\mathcal{H}} \psi d^3r + \lambda \int \psi^* \psi d^3r \right) = 0 \\ & \Rightarrow \int \delta \psi^* \hat{\mathcal{H}} \psi d^3r + \text{c.c.} + \lambda \int \delta \psi^* \psi d^3r + \text{c.c.} = 0 \\ & \Rightarrow \int \delta \psi^* [\hat{\mathcal{H}} + \lambda] \psi d^3r + \text{c.c.} = 0 \end{aligned}$$

$$\hat{\mathcal{H}} \psi = -\lambda \psi$$

The Lagrange multiplier is equal to the energy eigenvalue.

States whose expectation energy is stationary with respect to any variation in the wavefunction are the solutions of the Schrödinger equation.

■

- (2) Ground state energy: given a Hamiltonian  $\mathcal{H}$  with a discrete spectrum of eigenvalues whose lowest eigenvalue is  $\varepsilon_0$  and given any wave function  $\psi$ , we necessarily have

$$\langle \hat{\mathcal{H}} \rangle = \frac{\int \psi^* \hat{\mathcal{H}} \psi d^3r}{\int \psi^* \psi d^3r} \geq \varepsilon_0$$

PROOF:

$$\psi = \sum_i c_i \phi_i$$

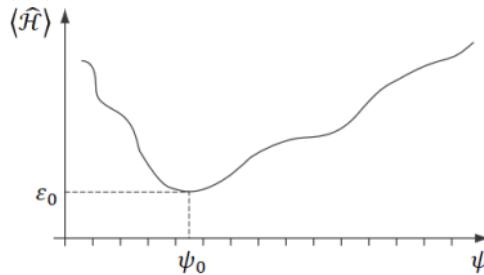
where  $\phi_i$  are orthonormal set of eigenfunctions of  $\hat{\mathcal{H}}$ .

$$\langle \psi | \hat{\mathcal{H}} | \psi \rangle = \frac{\sum_i \int c_i^* \phi_i^* \hat{\mathcal{H}} c_i \phi_i d^3r}{\sum_i \int c_i^* \phi_i^* c_i \phi_i d^3r} = \frac{\sum_i |c_i|^2 \varepsilon_i}{\sum_i |c_i|^2} = \varepsilon_0 + \frac{\sum_i |c_i|^2 (\varepsilon_i - \varepsilon_0)}{\sum_i |c_i|^2}$$

Since the second term is either positive or zero,  $\varepsilon_i \geq \varepsilon_0$ .

If the ground state is non-degenerate, the inequality is strict:

$\langle \hat{H} \rangle = \varepsilon_0$  only if  $\psi = \psi_0$



■

⇒ No trial function will have an expected energy value lower than the ground state energy of the system.

## B. HARTREE APPROXIMATION (1928)

### (1) Hartree product

The total wavefunction is a product of orthonormalized single-particle wavefunctions, called atomic orbitals.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \cdots \psi_N(\vec{r}_N)$$

where

$$\int \psi_i^*(\vec{r}_1)\psi_j(\vec{r}_1) d^3r_1 = \delta_{ij}$$

### (2) Hartree equation

$$\hat{H} = \sum_{i=1}^N \left( \frac{\hat{p}_i^2}{2m} + v_{\text{ion}}(\vec{r}_i) \right) + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N v_{\text{ee}}(\vec{r}_i, \vec{r}_j)$$

The expectation value of the energy is

$$\begin{aligned} \langle \hat{H} \rangle &= \int \psi_1^*(\vec{r}_1)\psi_2^*(\vec{r}_2) \cdots \hat{H}\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \cdots d^3r_1 d^3r_2 \cdots \\ &= \sum_i \int \psi_i^*(\vec{r}_i)\hat{H}(\vec{r}_i)\psi_i(\vec{r}_i) d^3r_i \\ &\quad + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N \int \psi_i^*(\vec{r}_i)\psi_j^*(\vec{r}_j)v_{\text{ee}}\psi_i(\vec{r}_i)\psi_j(\vec{r}_j) d^3r_i d^3r_j \end{aligned}$$

where

$$\hat{h}(\vec{r}_i) = \frac{\hat{p}_i^2}{2m} + v_{\text{ion}}(\vec{r}_i)$$

Renamed the dummy integration variables

$$\begin{aligned}\langle \hat{\mathcal{H}} \rangle &= \sum_i \int \psi_i^*(\vec{r}_1) \hat{h}(\vec{r}_1) \psi_i(\vec{r}_1) d^3 r_1 \\ &\quad + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N \int \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) v_{\text{ee}} \psi_i(\vec{r}_1) \psi_j(\vec{r}_2) d^3 r_1 d^3 r_2\end{aligned}$$

Use the Lagrange multiplier  $\varepsilon_k$

$$\begin{aligned}\delta \left( \langle \hat{\mathcal{H}} \rangle - \sum_k \varepsilon_k \int \psi_k^*(\vec{r}_1) \psi_k(\vec{r}_1) d^3 r_1 \right) &= 0 \\ \Rightarrow \sum_i \int \delta \psi_i^*(\vec{r}_1) \hat{h}(\vec{r}_1) \psi_i(\vec{r}_1) d^3 r_1 &\\ + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j \neq i}^N \int \delta \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) v_{\text{ee}} \psi_i(\vec{r}_1) \psi_j(\vec{r}_2) d^3 r_2 d^3 r_1 &\\ - \sum_k \int \delta \psi_k^*(\vec{r}_1) \varepsilon_k \psi_k(\vec{r}_1) d^3 r_1 + \text{c.c.} &= 0 \\ \Rightarrow \sum_k \int \delta \psi_k^*(\vec{r}_1) \left[ \hat{h}(\vec{r}_1) \psi_k(\vec{r}_1) \right. &\\ \left. + \frac{1}{2} \sum_{j \neq k} \int \psi_j^*(\vec{r}_2) v_{\text{ee}} \psi_k(\vec{r}_1) \psi_j(\vec{r}_2) d^3 r_2 - \varepsilon_k \psi_k(\vec{r}_1) \right] d^3 r_1 + \text{c.c.} &= 0\end{aligned}$$

Each pair  $j, k$  is counted only once.

$$\Rightarrow \hat{h}(\vec{r}_1) \psi_k(\vec{r}_1) + \frac{1}{2} \sum_{j \neq k} \int \psi_j^*(\vec{r}_2) v_{\text{ee}} \psi_k(\vec{r}_1) \psi_j(\vec{r}_2) d^3 r_2 - \varepsilon_k \psi_k(\vec{r}_1) = 0$$

The equation looks like a Schrödinger equation in which in addition to the Coulomb potential there is a Hartree potential:

$$v_H(\vec{r}_1) = \frac{1}{2} \int \sum_{j \neq k} \left| \psi_j(\vec{r}_2) \right|^2 v_{\text{ee}} d^3 r_2 = \frac{1}{2} \int n(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2$$

We obtain the Hartree equations ( $i = 1, \dots, N$ )

$$\Rightarrow \left[ \frac{\hat{p}_i^2}{2m} + v_{\text{ion}}(\vec{r}_1) + v_H(\vec{r}_1) \right] \psi_i(\vec{r}_1) = \varepsilon_i \psi_i(\vec{r}_1)$$

Each electron is governed by a single-particle Schrödinger equation

experiencing the Coulomb potential from the nuclei and from the  $N - 1$  other electrons.

OS:

In a real system, one electron feels the electric field induced by other electrons. This field varies with time  $t$ , because other electrons are moving. The Hartree approximation assumes that we can substitute this varying electric by its average value, which is time-independent. Therefore, in the Hartree approximation, we treat all other electrons as a static (not moving) and uniform background. This charge background generates a static field, which shifts the energy of our electron. Because we only consider the average field, this approximation is also known as the mean-field approximation.

## C. HARTREE-FOCK APPROXIMATION (1930)

- (1) The Slater determinant of  $N$  electrons wavefunction representation:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \psi_3(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \psi_3(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \psi_1(\vec{r}_3) & \psi_2(\vec{r}_3) & \psi_3(\vec{r}_3) & \cdots & \psi_N(\vec{r}_3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \psi_3(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

The exchange of two particles is equivalent to the exchange of two columns which produces a change of sign.

state representation:  $|\Psi\rangle = |\psi_1 \cdots \psi_N\rangle$

$|\Psi_p\rangle = |\psi_1 \cdots \psi_p \cdots \psi_N\rangle$  A wavefunction is differed by a single orbital

$|\Psi_{pq}\rangle = |\psi_1 \cdots \psi_p \psi_q \cdots \psi_N\rangle$  A wavefunction is differed by two orbitals

$|\Psi_{pqr}\rangle = |\psi_1 \cdots \psi_p \psi_q \psi_r \cdots \psi_N\rangle$  A wavefunction is differed by three orbitals

- (2) Slater-Condon rule

- Overlap integral

$$\langle \Psi | \Psi \rangle = 1$$

$$\langle \Psi | \Psi_p \rangle = 0$$

2. One-body operator

$$\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi \rangle = \sum_l \langle \psi_l(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_l(\vec{r}_1) \rangle$$

$$\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi_p \rangle = \langle \psi_m(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_p(\vec{r}_1) \rangle$$

$$\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi_{pq} \rangle = 0$$

One body operators have non zero matrix elements only between two determinantal wavefunctions which are either the same or differ in a single one particle wavefunction.

3. Two-body operator

$$\begin{aligned} \langle \Psi | \sum_{i < j}^N v_{ee} | \Psi \rangle = & \sum_{k < l}^N (\langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | v_{ee} | \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) \rangle \\ & - \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | v_{ee} | \psi_l(\vec{r}_1) \psi_k(\vec{r}_2) \rangle) \end{aligned}$$

$$\begin{aligned} \langle \Psi | \sum_{i < j}^N v_{ee} | \Psi_p \rangle = & \sum_l (\langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | v_{ee} | \psi_p(\vec{r}_1) \psi_l(\vec{r}_2) \rangle \\ & - \langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | v_{ee} | \psi_l(\vec{r}_1) \psi_p(\vec{r}_2) \rangle) \end{aligned}$$

$$\begin{aligned} \langle \Psi | \sum_{i < j}^N v_{ee} | \Psi_{pq} \rangle = & \langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | v_{ee} | \psi_p(\vec{r}_1) \psi_q(\vec{r}_2) \rangle \\ & - \langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | v_{ee} | \psi_q(\vec{r}_1) \psi_p(\vec{r}_2) \rangle \end{aligned}$$

$$\langle \Psi | \sum_{i < j}^N v_{ee} | \Psi_{pqr} \rangle = 0$$

Two body operators have non zero matrix elements only between two determinantal wavefunction which are either the same or differ at most in two one particle functions.

(3) Hartree-Fock equation

$$\begin{aligned} \hat{h}(\vec{r}_1) \psi_l(\vec{r}_1) + \frac{1}{2} \sum_{j \neq l} \int [ & \psi_j^*(\vec{r}_2) v_{ee} \psi_j(\vec{r}_2) \psi_l(\vec{r}_1) \\ & - \psi_j^*(\vec{r}_2) v_{ee} \psi_j(\vec{r}_1) \psi_l(\vec{r}_2) ] d^3 r_2 = \varepsilon_l \psi_l(\vec{r}_1) \end{aligned}$$

The self-interaction of an electron with itself in the bracket cancels out

$$\hat{h}(\vec{r}_1)\psi_l(\vec{r}_1) + \frac{1}{2} \sum_j \int \left[ \psi_j^*(\vec{r}_2)v_{ee}\psi_j(\vec{r}_2)\psi_l(\vec{r}_1) - \psi_j^*(\vec{r}_2)v_{ee}\psi_j(\vec{r}_1)\psi_l(\vec{r}_2) \right] d^3r_2 = \varepsilon_l\psi_l(\vec{r}_1)$$

Let the Hartree potential

$$v_H(\vec{r}_1) = \frac{1}{2} \sum_j \int \psi_j^*(\vec{r}_2) v(\vec{r}_1 - \vec{r}_2) \psi_j(\vec{r}_2) d^3r_2 = \frac{1}{2} \int \frac{e^2}{4\pi\epsilon_0} \frac{n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_2$$

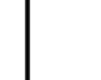
and the exchange potential (It is typical of a *nonlocal* interaction)

$$v_{ex}(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_j \psi_j^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{r}_1)$$

$$\Rightarrow \left[ \frac{\hat{p}_l^2}{2m} + v_{ion}(\vec{r}_1) + v_H(\vec{r}_1) \right] \psi_l(\vec{r}_1) - \int v_{ex}(\vec{r}_1, \vec{r}_2) \psi_l(\vec{r}_2) d^3r_2 = \varepsilon_l \psi_l(\vec{r}_1)$$

Hartree-Fock approximation introduces an effective one-particle problem by considering a single particle in a mean-field potential generated by all other particles.

- (4) Restricted Hartree-Fock and unrestricted Hartree-Fock calculations:  
The wavefunctions are composed of two groups, spin-up and spin-down functions which have the same spatial wavefunctions.

 For two well-separated H <sub>1</sub> atoms, unrestricted H-F are necessary.	 For two electrons in He, one can use restricted H-F.
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## D. HARTREE-FOCK APPROXIMATION FOR THE JELLIUM MODEL

- (1) Hartree-Fock eigenstates:

For the jellium model, we do not have a periodic potential and because there is invariance to all translations, the symmetry dictates that momentum is a good quantum number and therefore, the Hartree-Fock single electron states are characterized by  $\vec{k}$ , and the Hartree-Fock eigenstates must be plane-waves,

$$\psi_i(\vec{r}) = \frac{e^{i\vec{k} \cdot \vec{r}}}{\sqrt{\nu}}$$

OS:

If the positive ions were located on a lattice, the average distribution of electrons in the unit cell would be more "spread around" than that of the positive ionic charge. So there would be a periodically modulated difference which would mean that the electron wavefunctions are Bloch states, not plane-waves, and solving for those makes this really complicated.

The allowed momenta  $\vec{k}$  are dictated by the size of the box  $\mathcal{V} = L^3$ , e.g.,

$$k_x = \frac{2\pi}{L} n_x, \quad n_x = 0, \pm 1, \pm 2, \dots$$

There is no restriction to a Brillouin zone because we have invariance to full translations, not to a discrete lattice group. Any momentum with components of this type is allowed, and in the limit  $V \rightarrow \infty$  all momenta become allowed.

Assume a paramagnetic ground state, i.e. one with equal number of spin-up and spin-down electrons, then the Fermi momentum  $\vec{k}_F$  is defined such that precisely  $N$  states are occupied, i.e.,

$$N = \sum_{|\vec{k}| < k_F} 1$$

In the limit  $\mathcal{V} \rightarrow \infty$ , we have

$$k_F = (3\pi^2 n)^{1/3}, \quad n = \frac{N}{\mathcal{V}}$$

(2) Hartree-Fock eigenenergies:

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} - \varepsilon_{\text{ex}}(\vec{k})$$

The exchange energy (Fock term), which lowers the energy from that of a free electron is

$$\begin{aligned}
\varepsilon_{\text{ex}}(\vec{k}) &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \psi_l^*(\vec{r}_1) \sum_j \psi_j^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{r}_1) \psi_l(\vec{r}_2) d^3 r_1 d^3 r_2 \\
&= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{k'} \int \int \frac{e^{-i\vec{k}\cdot\vec{r}_1}}{\sqrt{\mathcal{V}}} \frac{e^{-i\vec{k}'\cdot\vec{r}_2}}{\sqrt{\mathcal{V}}} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \frac{e^{i\vec{k}'\cdot\vec{r}_1}}{\sqrt{\mathcal{V}}} \frac{e^{i\vec{k}\cdot\vec{r}_2}}{\sqrt{\mathcal{V}}} d^3 r_1 d^3 r_2 \\
&= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{\mathcal{V}^2} \sum_{k'} \int \int \frac{e^{-i(\vec{k}-\vec{k}')\cdot(\vec{r}_1-\vec{r}_2)}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2
\end{aligned}$$

Let  $\vec{r} = \vec{r}_1 - \vec{r}_2$

$$\varepsilon_{\text{ex}}(\vec{k}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{k'} \frac{1}{\mathcal{V}} \int \frac{e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}}{|\vec{r}|} d^3 r = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{\mathcal{V}} \sum_{k'} \frac{4\pi}{|\vec{k} - \vec{k}'|^2}$$

OS:

$$\begin{aligned}
\int \frac{e^{i\vec{k}\cdot\vec{r}}}{r} d^3 r &= 2\pi \int \frac{e^{ikr \cos \theta}}{r} r^2 dr d(\cos \theta) \\
&= \frac{2\pi}{ik} \int_0^\infty [e^{ikr} - e^{-ikr}] dr \\
&= \frac{2\pi}{ik} \lim_{\alpha \rightarrow 0} \int_0^\infty [e^{ikr} - e^{-ikr}] e^{-\alpha r} dr \\
&= \frac{2\pi}{ik} \lim_{\alpha \rightarrow 0} \left[ \frac{e^{(-\alpha+ik)r}}{-\alpha + ik} - \frac{e^{(-\alpha-ik)r}}{\alpha + ik} \right]_0^\infty \\
&= \frac{2\pi}{ik} \lim_{\alpha \rightarrow 0} \left[ \frac{1}{\alpha - ik} - \frac{1}{\alpha + ik} \right] \\
&= \frac{2\pi}{ik} \frac{2i}{k} = \frac{4\pi}{k^2}
\end{aligned}$$

$$\begin{array}{ccc}
\text{Coulomb repulsion} & & \text{Fourier transform} \\
\Rightarrow \quad \frac{1}{r} & \rightarrow & \frac{4\pi}{k^2}
\end{array}$$

In the thermodynamic limit

$$\begin{aligned}
\varepsilon_{\text{ex}}(\vec{k}) &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{(2\pi)^3} \int \frac{1}{|\vec{k} - \vec{k}'|^2} d^3 k' \\
&= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi} \left[ 2k_F + \frac{k_F^2 - k^2}{k} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]
\end{aligned}$$

OS:

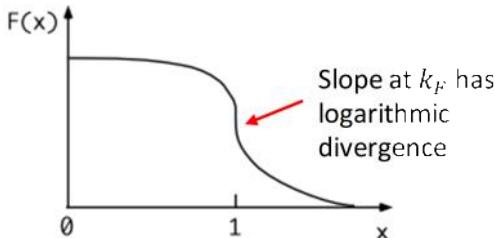
$$\begin{aligned} \int \frac{1}{|\vec{k} - \vec{k}'|^2} d^3 k' &= 2\pi \int_0^{k_F} \int_{-1}^1 \frac{1}{k^2 - 2kk' \cos \theta + k'^2} k'^2 dk' d(\cos \theta) \\ &= \frac{\pi}{k} \int_0^{k_F} \ln \left| \frac{k+k'}{k-k'} \right| k' dk' \\ &= \pi \left[ 2k_F + \frac{k_F^2 - k^2}{k} \ln \left| \frac{k_F+k}{k_F-k} \right| \right] \end{aligned}$$

$$\varepsilon_{\text{ex}}(\vec{k}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{4k_F}{2\pi} F\left(\frac{k}{k_F}\right) = \frac{e^2}{4\pi\epsilon_0} \frac{k_F}{\pi} F\left(\frac{k}{k_F}\right)$$

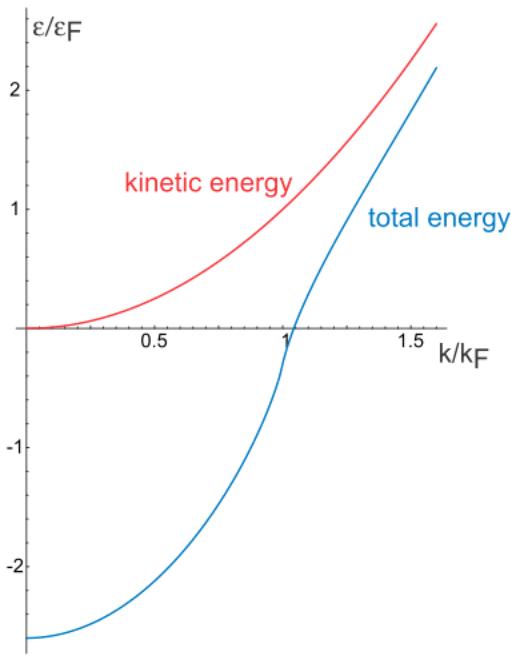
where

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|, \quad x = \frac{k}{k_F}$$

is the Lindhard dielectric function in bulk metal.



$$\begin{aligned} F(1) &= \frac{1}{2} \\ \Rightarrow \varepsilon_k &= \frac{\hbar^2 k^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{k_F}{\pi} F\left(\frac{k}{k_F}\right) \end{aligned}$$



The exchange interaction substantially lowers the energy.

## E. STABILITY OF HARTREE-FOCK

- (1) Charge neutrality: In jellium model, the negative charge of the electrons is compensated by a positively charged background of ions.

**PROOF:**

$$\begin{aligned}
 \text{Let } n &= \frac{Z}{V_c} = \frac{N}{\mathcal{V}} \\
 \varepsilon_H &= \frac{1}{2} \int \int \frac{e^{-i\vec{k} \cdot \vec{r}_1}}{\sqrt{\mathcal{V}}} \frac{e^2}{4\pi\epsilon_0} \frac{n}{|\vec{r}_1 - \vec{r}_2|} \frac{e^{i\vec{k} \cdot \vec{r}_1}}{\sqrt{\mathcal{V}}} d^3 r_1 d^3 r_2 \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \frac{1}{\mathcal{V}} \frac{n}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2 \\
 v_{\text{ion}} &= - \sum_{I=1}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\vec{r} - \vec{R}_I|} = - \frac{e^2}{4\pi\epsilon_0} \int \frac{n}{|\vec{r}_i - \vec{R}|} d^3 R
 \end{aligned}$$

$$\begin{aligned}
\varepsilon_{\text{ion}} &= -\frac{e^2}{4\pi\epsilon_0} \int \int \frac{e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{\mathcal{V}}} \frac{n}{|\vec{r} - \vec{R}|} \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\mathcal{V}}} d^3R d^3r \\
&= -\frac{e^2}{4\pi\epsilon_0} \int \int \frac{1}{\mathcal{V}} \frac{n}{|\vec{r} - \vec{R}|} d^3R d^3r \\
V_{\text{ii}} &= \frac{1}{2} \sum_{I=1}^{N-1} \sum_{J \neq I}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \frac{n^2}{|\vec{R} - \vec{R}'|} d^3R d^3R' \\
E_{\text{ii}} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \frac{n^2}{|\vec{R} - \vec{R}'|} d^3R d^3R'
\end{aligned}$$

The total electro-static energy of  $N$  electron gas

$$E_{\text{ion}} + E_{\text{H}} + E_{\text{ii}} = \sum_i (\varepsilon_{\text{ion}} + \varepsilon_{\text{H}}) + E_{\text{ii}} = 0 \Rightarrow \text{charge neutrality}$$

■

(2) Pair correlation function (two-particle correlation function):

The energy resulting from the Coulomb repulsion between the electrons

$$\begin{aligned}
E_{\text{HF}} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \frac{\sum_{i,j \neq i} \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \psi_j(\vec{r}_1) \psi_i(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 \\
&= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \frac{\sum_{i,j} \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \psi_j(\vec{r}_1) \psi_i(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2
\end{aligned}$$

Let the pair correlation function

$$\begin{aligned}
&\sum_{i,j} \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \psi_j(\vec{r}_1) \psi_i(\vec{r}_2) \\
&= 2 \sum_{kk'qq'} \frac{e^{-i\vec{q}\cdot\vec{r}_1}}{\sqrt{\mathcal{V}}} \frac{e^{-i\vec{k}\cdot\vec{r}_2}}{\sqrt{\mathcal{V}}} \frac{e^{i\vec{k}'\cdot\vec{r}_1}}{\sqrt{\mathcal{V}}} \frac{e^{i\vec{q}'\cdot\vec{r}_2}}{\sqrt{\mathcal{V}}} \chi_{q\sigma'} \chi_{k\sigma} \chi_{k'\sigma} \chi_{q'\sigma'} \\
&= \frac{2}{V^2} \sum_{kk'qq'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_1} e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}_2} \chi_{q\sigma'} \chi_{k\sigma} \chi_{k'\sigma} \chi_{q'\sigma'}
\end{aligned}$$

1. Consider anti-parallel spins  $\sigma \neq \sigma'$ :

$$\chi_{q\sigma'} \chi_{k\sigma} \chi_{k'\sigma} \chi_{q'\sigma'} = \delta_{kk'} \delta_{qq'}$$

$$\begin{aligned}
\frac{2}{V^2} \sum_{kk'qq'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_1} e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}_2} \delta_{kk'} \delta_{qq'} &= \frac{2}{V^2} \sum_{kq} \frac{1}{2} \\
&= \frac{2}{V^2} \left( \frac{N}{2} \right)^2 \\
&= \frac{n^2}{2}
\end{aligned}$$

2. Consider parallel spins  $\sigma = \sigma'$ :

$$\begin{aligned}
\chi_{q\sigma'} \chi_{k\sigma} \chi_{k'\sigma} \chi_{q'\sigma'} &= \delta_{kk'} \delta_{qq'} - \delta_{kq'} \delta_{k'q} \\
\frac{2}{V^2} \sum_{kk'qq'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_1} e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}_2} &\left( \delta_{kk'} \delta_{qq'} - \delta_{kq'} \delta_{k'q} \right) \\
&= \frac{2}{V^2} \sum_{kq} \left( \frac{1}{2} - e^{-i(\vec{k}-\vec{q})\cdot\vec{r}_1} e^{-i(\vec{q}-\vec{k})\cdot\vec{r}_2} \right) \\
&= \frac{n^2}{2} - \frac{2}{V^2} \sum_{kq} e^{-i(\vec{k}-\vec{q})\cdot(\vec{r}_1-\vec{r}_2)}
\end{aligned}$$

The pair correlation function becomes

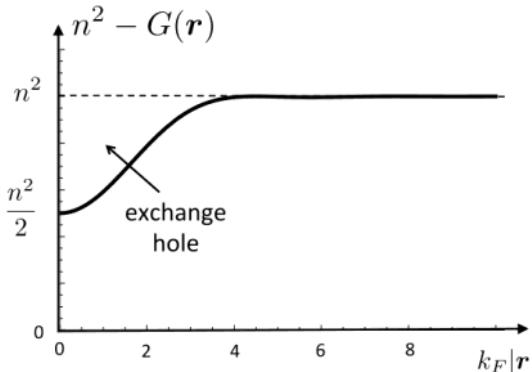
$$\sum_{i,j} \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \psi_j(\vec{r}_1) \psi_i(\vec{r}_2) = n^2 - \frac{2}{V^2} \sum_{kq} e^{-i(\vec{k}-\vec{q})\cdot(\vec{r}_1-\vec{r}_2)}$$

$$\text{Let } G(\vec{r}_1, \vec{r}_2) = \frac{2}{V^2} \sum_{kq} e^{-i(\vec{k}-\vec{q})\cdot(\vec{r}_1-\vec{r}_2)} \text{ and } \vec{r} = \vec{r}_2 - \vec{r}_1$$

$$\begin{aligned}
G(\vec{r}) &= 2 \left( \frac{1}{V} \sum_k e^{i\vec{k}\cdot\vec{r}} \right)^2 \\
&= 2 \left( \frac{1}{(2\pi)^3} \int_{|\vec{k}| \leq k_F} e^{i\vec{k}\cdot\vec{r}} d^3k \right)^2 \\
&= \left( \frac{1}{2\pi^2 r} \int_0^{k_F} \sin kr k dk \right)^2 \\
&= 2 \left( \frac{1}{2\pi^2} \frac{\sin k_F r - k_F r \cos k_F r}{r^3} \right)^2 \\
&= \frac{n^2}{2} \left( 3 \frac{\sin k_F r - k_F r \cos k_F r}{(k_F r)^3} \right)^2
\end{aligned}$$

Hartree-Fock tells us that the average electron density that an electron that is at  $\vec{r}_1$  sees at distance  $\vec{r}_2 = \vec{r}_1 + \vec{r}$ , i.e., at relative distance  $\vec{r}$  from

where it is.



The average density is reduced to  $n^2/2$  as  $r \rightarrow 0$ , showing that the electron repulses other electrons with the same spin (because of the Pauli principle), from its immediate neighborhood. The charge is thus rearranged and we can see some long-range oscillations because of this rearrangement.

OS:

$$\begin{aligned} \lim_{x \rightarrow 0} \frac{\sin x - x \cos x}{x^3} &= \lim_{x \rightarrow 0} \frac{\cos x - \cos x + x \sin x}{3x^2} \\ &= \frac{1}{3} \lim_{x \rightarrow 0} \frac{\sin x}{x} \\ &= \frac{1}{3} \lim_{x \rightarrow 0} \frac{\cos x}{1} = \frac{1}{3} \\ \lim_{x \rightarrow \infty} \frac{\sin x - x \cos x}{x^3} &= 0 \end{aligned}$$

- (3) The total ground state Hartree-Fock energy is

$$\begin{aligned} E &= E_{\text{kin}} + E_{\text{Fock}} \\ E_{\text{kin}} &= 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m} \\ &= 2 \frac{\mathcal{V}}{(2\pi)^3} \int \frac{\hbar^2 k^2}{2m} d^3 k \\ &= 2 \frac{\mathcal{V}}{(2\pi)^3} \int \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk \\ &= \frac{\mathcal{V}\hbar^2}{2m\pi^2} \frac{k_F^5}{5} \\ &= \frac{3N}{5} \frac{\hbar^2 k_F^2}{2m} \end{aligned}$$

$$E_{\text{Fock}} = -2 \frac{e^2}{4\pi\epsilon_0} \frac{k_F}{\pi} \sum_{k < k_F} F\left(\frac{k}{k_F}\right) = ?$$

Alternative approach:

$$E_{\text{Fock}} = -\mathcal{V} \frac{9n^2}{4} \frac{e^2}{4\pi\epsilon_0} \int \frac{1}{|\vec{r}|} \left( \frac{\sin k_F r - k_F r \cos k_F r}{(k_F r)^3} \right)^2 d^3r = -\frac{e^2}{4\pi\epsilon_0} \frac{3Nk_F}{4\pi}$$

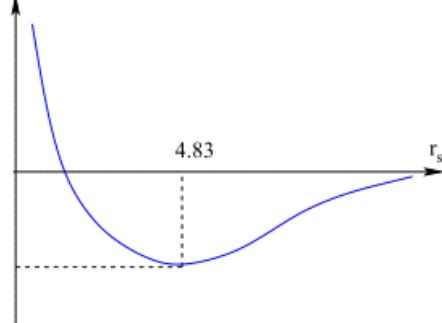
OS:

$$\int \frac{1}{x} \left( \frac{\sin x - x \cos x}{x^3} \right)^2 d^3x = \int_0^\infty x \left( \frac{\sin x - x \cos x}{x^3} \right)^2 dx = \frac{1}{4}$$

The total energy per electron is

$$\frac{E}{N} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{3k_F}{4\pi} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s}$$

E/N



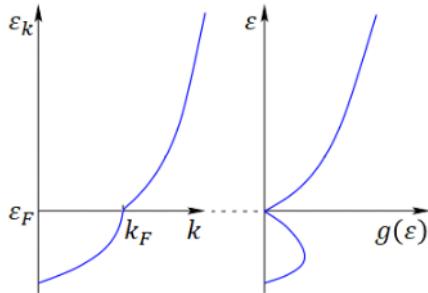
This estimate is roughly in agreement with the Alkali metals. The delocalized electrons are responsible for the cohesion of the positive background yielding a stable solid. The metal is stable in HF approximation.

## F. FAILURE OF HF APPROXIMATION

G. Eigenenergy  $\varepsilon_k$  and density of states  $g(\varepsilon)$

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{2\pi^2 \epsilon_0} F\left(\frac{k}{k_F}\right)$$

$$\begin{aligned}
g(\varepsilon) &= \frac{1}{V} \sum_k \delta(\varepsilon - \varepsilon_k) \\
&= \frac{1}{(2\pi)^3} \int \delta(\varepsilon - \varepsilon_k) d^3k \\
&= \frac{1}{\pi^2} \int_0^\infty \delta(\varepsilon - \varepsilon_k) k^2 dk
\end{aligned}$$



1. The energy dispersion has a logarithmic singularity in the slope at  $k = k_F$

The Fermi velocity is

$$v_F = \left. \frac{\partial \varepsilon(\vec{k})}{\partial \vec{k}} \right|_{k_F} = \frac{\hbar^2 k_F}{m} + \infty = \infty$$

2. The density of states at the Fermi level is zero called Coulomb gap.

$$g(\varepsilon_F) \approx \frac{1}{v_F} \rightarrow 0$$

However, in good clean metals, there is a large DOS at the Fermi energy.

- (1) The failure of the HF approximation for jellium is caused by the nonlocality of exchange operator (Fock term).

The Linhard function  $F(x)$  has a log divergence in its slope at  $k = k_F$ , the DOS vanishes at the Fermi energy. This gap at the Fermi energy (known as Coulomb gap) is attributed to the Coulomb repulsion, in which case  $4\pi/k^2$ . In other words, the  $1/r$  Coulomb potential (long-range interaction) leads to the singularity at  $k_F$  which resulted in gap in the DOS.

- (2) If we have a form that did not diverge as  $k \rightarrow k_F$ , there would

be avoided. However, that would mean that the Coulomb interaction is not long-range,  $1/r$ -like. We expect some short-range interactions between electrons, but the long range parts should definitely vanish much faster than  $1/r$ .

# 8-3 Random Phase Approximation

Tuesday, December 20, 2011      8:30 PM

## A. SCREENING

### (1) Screening:

Suppose a positively charged particle density  $\rho_{\text{ext}}(\vec{r})$  is placed at a given position in the electron gas and rigidly held there. It will attract electrons, creating a surplus of negative charge density in its neighborhood  $\rho_{\text{ind}}(\vec{r})$ .  $V(\vec{r})$  is produced by both the positively charged particle and the cloud of screening electrons it induces.

The Poisson's equations:

$$\nabla^2 V_{\text{ext}}(\vec{r}) = -\frac{\rho_{\text{ext}}(\vec{r})}{\epsilon_0}$$
$$\nabla^2 V(\vec{r}) = -\frac{\rho_{\text{ext}}(\vec{r}) + \rho_{\text{ind}}(\vec{r})}{\epsilon_0} = -\frac{\rho(\vec{r})}{\epsilon_0}$$

### (2) Dielectric function:

1. In general, the phenomenon, where the total potential seen by an individual electron is less than the external potential, is incorporated into electromagnetic theory through the dielectric function  $\epsilon$ ,

$$\vec{D}(\vec{r}) = \epsilon_0 \int \epsilon(\vec{r}, \vec{r}') \vec{E}(\vec{r}') d\vec{r}',$$

where the electric displacement  $\vec{D}$  is generated by "free" charge (i.e.  $\rho_{\text{ext}}$ ) and the electric field  $\vec{E}$  by the total charges (i.e.  $\rho$ ).

Rewrite the equation in terms of the potentials generated by those charge distributions:

$$V_{\text{ext}}(\vec{r}) = \epsilon_0 \int \epsilon(\vec{r}, \vec{r}') V(\vec{r}') d\vec{r}'$$

In a spatially uniform electron gas,  $\epsilon$  depends only on the separation between coordinates, i.e.,  $\epsilon(\vec{r}, \vec{r}') = \epsilon(\vec{r} - \vec{r}')$  and

$$V_{\text{ext}}(\vec{r}) = \epsilon_0 \int \epsilon(\vec{r} - \vec{r}') V(\vec{r}') d\vec{r}'.$$

The equation becomes a convolution in real space - better written of course in Fourier (momentum) space as

$$V_{\text{ext}}(\vec{q}) = \epsilon_0 \epsilon(\vec{q}) V(\vec{q})$$

**PROOF:**

$$\begin{aligned} V_{\text{ext}}(\vec{q}) &= \int V_{\text{ext}}(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} dr \\ &= \epsilon_0 \int \epsilon(\vec{r} - \vec{r}') V(\vec{r}') e^{-i\vec{q}\cdot\vec{r}} dr' dr \\ &= \epsilon_0 \int \frac{1}{V} \sum_{q'} \epsilon(\vec{q}') e^{i\vec{q}'\cdot(\vec{r}-\vec{r}')} \frac{1}{V} \sum_{q''} V(\vec{q}'') e^{i\vec{q}''\cdot\vec{r}'} e^{-i\vec{q}\cdot\vec{r}} dr' dr \\ &= \epsilon_0 \sum_{q', q''} \epsilon(\vec{q}') V(\vec{q}'') \frac{1}{V} \int e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}} dr \\ &\quad \times \frac{1}{V} \int e^{-i(\vec{q}'-\vec{q}'')\cdot\vec{r}'} dr' \\ &= \epsilon_0 \sum_{q', q''} \epsilon(\vec{q}') V(\vec{q}'') \delta_{q', q''} \delta_{q', q''} \\ &= \epsilon_0 \epsilon(\vec{q}) V(\vec{q}) \end{aligned}$$

■

2. Assume  $V(\vec{r})$  is weak enough to produce a linear response, i.e.,  $\rho_{\text{ind}}$  and  $V$  are linearly related. Their Fourier transformations satisfy a relation of the form:

$$\rho_{\text{ind}}(\vec{q}) = \chi(\vec{q}) V(\vec{q}) \Rightarrow \epsilon(\vec{q}) = 1 - \frac{\chi(\vec{q})}{\epsilon_0 q^2}$$

where  $\Pi_{\text{sc}}(\vec{q})$  is the "screened" density response function.

**PROOF:**

The Fourier transform of the Poisson equation is

$$\begin{aligned} \nabla^2 V(\vec{r}) &= -\frac{\rho(\vec{r})}{\epsilon_0} \\ \nabla^2 \frac{1}{V} \sum_q V(\vec{q}) e^{i\vec{q}\cdot\vec{r}} &= -\frac{1}{\epsilon_0} \frac{1}{V} \sum_q \rho(\vec{q}) e^{i\vec{q}\cdot\vec{r}} \\ \sum_q q^2 V(\vec{q}) e^{i\vec{q}\cdot\vec{r}} &= \frac{1}{\epsilon_0} \sum_q \rho(\vec{q}) e^{i\vec{q}\cdot\vec{r}} \\ q^2 V(\vec{q}) &= \frac{\rho(\vec{q})}{\epsilon_0} \end{aligned}$$

Similarly,

$$q^2 V_{\text{ext}}(\vec{q}) = \frac{\rho_{\text{ext}}(\vec{q})}{\epsilon_0}$$

The density response function:

$$q^2 V(\vec{q}) = \frac{\rho(\vec{q})}{\epsilon_0} = \frac{\rho_{\text{ext}}(\vec{q}) + \rho_{\text{ind}}(\vec{q})}{\epsilon_0} = q^2 V_{\text{ext}}(\vec{q}) + \frac{\chi(\vec{q}) V(\vec{q})}{\epsilon_0}$$

$$V_{\text{ext}}(\vec{q}) = \left[ 1 - \frac{\chi(\vec{q})}{\epsilon_0 q^2} \right] V(\vec{q}) = \epsilon(\vec{q}) V(\vec{q}) \Rightarrow \epsilon(\vec{q}) = 1 - \frac{\chi(\vec{q})}{\epsilon_0 q^2}$$

■

## B. THOMAS-FERMI APPROXIMATION

- (1) In principle, to find the charge density in the presence of  $V(\vec{r}) = V_{\text{ext}}(\vec{r}) + V_{\text{ind}}(\vec{r})$ , we solve the one-electron Schrödinger equation (Hartree equation),

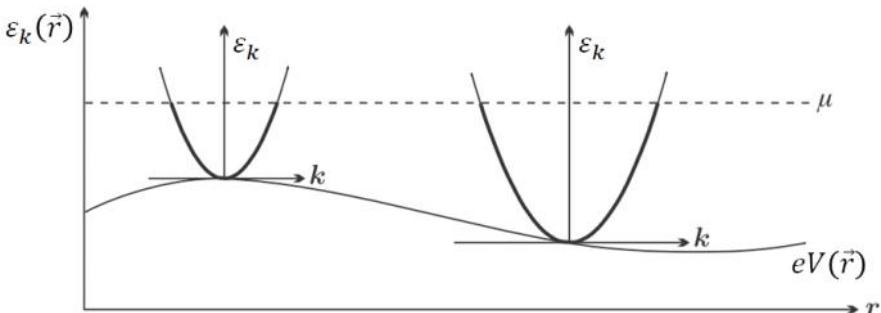
$$\left[ \frac{\hat{p}_i^2}{2m} - eV(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

and then construct the electronic density from the one-electron wave function using

$$\rho(\vec{r}) = -e \sum_i |\psi_i(\vec{r})|^2$$

- (2) Assume that  $V(\vec{r})$  is slowly varying enough on the scale of the Fermi wavelength  $2\pi/k_F$  that the energy eigenvalues  $E_i$  are still indexed by momentum, but just shifted locally by the potential:

$$\varepsilon_k(\vec{r}) = \varepsilon_k - eV(\vec{r}) = \frac{\hbar^2 k^2}{2m} - eV(\vec{r})$$



- (3) The electron number density in the presence of the total potential  $V(\vec{r})$

$$n(\vec{r}) = \frac{1}{V} \sum_k \frac{1}{e^{\beta(\hbar^2 k^2/2m - eV(\vec{r}) - \mu)} + 1}$$

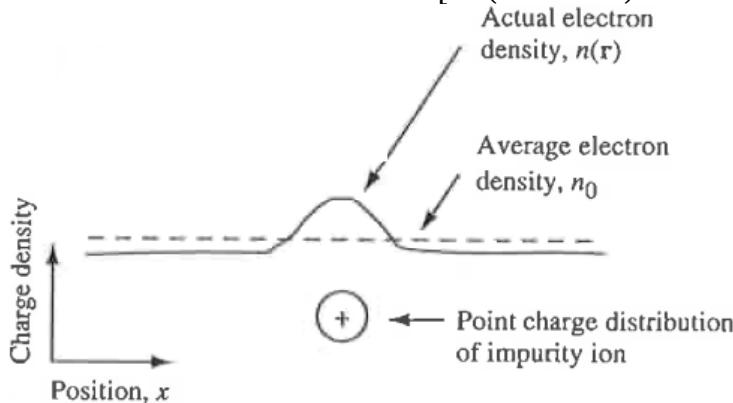
$$= \frac{1}{(2\pi)^3} \int \frac{1}{e^{\beta(\hbar^2 k^2/2m - eV(\vec{r}) - \mu)} + 1} d^3k$$

The electron number density of the uniform positive background

$$n_0(\mu) = \frac{1}{(2\pi)^3} \int \frac{1}{e^{\beta(\hbar^2 k^2/2m - \mu)} + 1} d^3k$$

The induced charge density

$$\rho_{\text{ind}}(\vec{r}) = -e[n(\vec{r}) - n_0(\mu)] = -e[n_0(\mu + eV(\vec{r})) - n_0(\mu)]$$



If  $V(\vec{r}) \ll 1$

$$\rho_{\text{ind}}(\vec{r}) \approx -e^2 \frac{\partial n_0}{\partial \mu} V(\vec{r})$$

$$\Rightarrow \chi(\vec{q}) = -e^2 \frac{\partial n_0}{\partial \mu} \dots \text{independent of } \vec{q}$$

(4) The Thomas-Fermi dielectric function

$$\epsilon(\vec{q}) = 1 - \frac{\chi(\vec{q})}{\epsilon_0 q^2} = 1 + \frac{e^2}{\epsilon_0 q^2} \frac{\partial n_0}{\partial \mu}$$

Define a Thomas-Fermi wave vector  $k_0$

$$k_0^2 = e^2 \frac{\partial n_0}{\partial \mu}$$

$$\Rightarrow \epsilon(\vec{q}) = 1 + \frac{k_0^2}{\epsilon_0 q^2}$$

EXAMPLES:

If the external charge is an electron, then

$$\begin{aligned}\rho_{\text{ext}}(\vec{r}) &= -e\delta(\vec{r}) \\ \Rightarrow \nabla^2 V_{\text{ext}}(\vec{r}) &= -\frac{(-e\delta(\vec{r}))}{\epsilon_0} \\ \Rightarrow V_{\text{ext}}(\vec{r}) &= \frac{e}{4\pi\epsilon_0 r} \xrightarrow{\text{Fourier Transform}} V_{\text{ext}}(\vec{k}) = \frac{e}{\epsilon_0 k^2}\end{aligned}$$

The total potential inside the solid is

$$V(\vec{k}) = \frac{V_{\text{ext}}(\vec{k})}{\epsilon(\vec{k})} = \frac{e}{\epsilon_0 \epsilon(\vec{k}) k^2} = \frac{e}{\epsilon_0} \frac{1}{k^2 + k_0^2}$$

The Fourier transform is

$$\begin{aligned}V(\vec{r}) &= \frac{e}{\epsilon_0} \sum_k \frac{1}{k^2 + k_0^2} e^{i\vec{k} \cdot \vec{r}} \\ &= \frac{e}{\epsilon_0 (2\pi)^3} \int \frac{e^{i\vec{k} \cdot \vec{r}}}{k^2 + k_0^2} d^3 k \\ &= \frac{e}{\epsilon_0 (2\pi)^3} \int_0^\infty \frac{k^2}{k^2 + k_0^2} dk \int_0^\pi e^{ikr \cos \theta} \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{e}{\epsilon_0 (2\pi)^2} \int_0^\infty \frac{k^2}{k^2 + k_0^2} dk \int_{-1}^1 e^{ikrx} dx \\ &= \frac{2e}{\epsilon_0 (2\pi)^2} \int_0^\infty \frac{k^2}{k^2 + k_0^2} dk \frac{i \sin kr}{ikr} \\ &= \frac{e}{\epsilon_0 (2\pi)^2 r} \int_{-\infty}^\infty \frac{k \sin kr}{k^2 + k_0^2} dk\end{aligned}$$

Since

$$\int_{-\infty}^\infty \frac{ke^{ikr}}{k^2 + k_0^2} dk = 2\pi i \frac{ik_0 e^{-k_0 r}}{2ik_0} = i\pi e^{-k_0 r}$$

Take the imaginary part,

$$V(\vec{r}) = \frac{e}{4\pi\epsilon_0 r} e^{-k_0 r}$$

This is known as a screen Coulomb or Yukawa potential, with a screening length of  $1/k_0$ .

$$\begin{aligned}\text{If } T \ll T_F, \quad k_F &= (3\pi^2 n_0)^{1/3}, \quad \mu = \frac{\hbar^2 k_F^2}{2m} \\ \Rightarrow k_F^2 &= (3\pi^2 n_0)^{2/3} = \frac{2m\mu}{\hbar^2} \Rightarrow n_0 = \left(\frac{2m\mu}{\hbar^2}\right)^{3/2} \frac{1}{3\pi^2}\end{aligned}$$

$$\Rightarrow \frac{\partial n_0}{\partial \mu} = \frac{3}{2} \frac{2m}{\hbar^2} \sqrt{\frac{2m\mu}{\hbar^2}} \frac{1}{3\pi^2} = \frac{3}{2} \frac{2m}{\hbar^2} \sqrt{k_F^2} \frac{1}{3\pi^2} = \frac{mk_F}{\pi^2 \hbar^2}$$

$$\text{Define } k_0^2 = e^2 \frac{\partial n_0}{\partial \mu} = \frac{me^2 k_F}{\pi^2 \hbar^2} = \frac{k_F}{\pi^2 a_0}$$

For metal,  $k_0$  is of the order of  $k_F$ , i.e., disturbances are screened in a distance similar to the interparticle spacing. Thus the electrons are highly effective in shielding external charges.

## C. RANDOM PHASE APPROXIMATION

- (1) Consider a free electron gas

$$\hat{H}_0 |\psi_k\rangle = \varepsilon_k |\psi_k\rangle, \quad \langle \vec{r} | \psi_k \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

and the system is subject to a time-dependent perturbation as

$$V(\vec{r}, t) = \sum_k V_k e^{i\vec{k} \cdot \vec{x}} e^{\epsilon t}$$

where  $\vec{k} \cdot \vec{x} = (\vec{q} \cdot \vec{r} - \omega t)$  and  $\epsilon \rightarrow 0$  which ensures that the perturbation vanished at  $t = -\infty$ .

The time-dependent perturbed state is given

$$|\Psi_k(t)\rangle = \sum_{k'} c_{k'}^{(0)}(t) e^{-i\omega_{k'} t} |\psi_k\rangle + \sum_{k'} c_{k'}^{(1)}(t) e^{-i\omega_{k'} t} |\psi_{k'}\rangle \\ + \sum_{k'} c_{k'}^{(2)}(t) e^{-i\omega_{k'} t} |\psi_{k'}\rangle + \dots$$

where the zeroth-order term:

$$c_{k'}^{(0)}(t) = \delta_{k'k}$$

the first-order term:

$$c_{k'}^{(1)}(t) = -\frac{i}{\hbar} \int_{-\infty}^t V_{k'k}(t') e^{i\omega_{k'} t'} dt'$$

and the second-order term:

$$c_{k'}^{(2)}(t) = -\frac{1}{\hbar^2} \sum_{k'' \neq k} \int_{-\infty}^t \int_{-\infty}^{t'} V_{k'k''}(t') V_{k''k}(t'') e^{i\omega_{k'k''} t'} e^{i\omega_{k''k} t''} dt'' dt'$$

- (2) Consider the perturbed state up to the first-order and ignore the second-order term. Thus we only need to consider the term

$$V_{k'k}(t') = \langle \psi_{k'} | (-e) V(\vec{r}, t') | \psi_k \rangle = -e \sum_k \left\langle \psi_{k'} \middle| V_k e^{i\vec{k} \cdot \vec{x}} \right| \psi_k \rangle e^{\epsilon t'}$$

Assume that the phases are random and the electrons response to the Fourier components  $e^{i\vec{q} \cdot \vec{r}}$  independently. Thus, the perturbation term can be simplified as

$$V(\vec{r}, t') = \frac{V}{\mathcal{V}} \left( e^{i\vec{q} \cdot \vec{r}} e^{-i\omega t'} e^{\epsilon t'} + e^{-i\vec{q} \cdot \vec{r}} e^{i\omega t'} e^{\epsilon t'} \right)$$

$$= v e^{i\vec{q} \cdot \vec{r}} e^{-i\omega t'} e^{\epsilon t'} + v e^{-i\vec{q} \cdot \vec{r}} e^{i\omega t'} e^{\epsilon t'}$$

$$V_{k'k}(t') = -ev \left\langle \psi_{k'} \middle| e^{i\vec{q} \cdot \vec{r}} \right| \psi_k \rangle e^{i(-\omega - i\epsilon)t'} - ev \left\langle \psi_{k'} \middle| e^{-i\vec{q} \cdot \vec{r}} \right| \psi_k \rangle e^{i(\omega - i\epsilon)t'}$$

$$\begin{aligned} \left\langle \psi_{k'} \middle| v e^{i\vec{q} \cdot \vec{r}} \right| \psi_k \rangle &= \frac{1}{\mathcal{V}} \int \left\langle \psi(\vec{r}') \middle| e^{i\vec{q} \cdot \vec{r}} \right| \psi(\vec{r}) \rangle e^{-i\vec{k}' \cdot \vec{r}'} e^{i\vec{k} \cdot \vec{r}} d^3 r' d^3 r \\ &= \frac{1}{\mathcal{V}} \int \delta(\vec{r}' - \vec{r}) e^{-i\vec{k}' \cdot \vec{r}'} e^{i\vec{k} \cdot \vec{r}} e^{i\vec{q} \cdot \vec{r}} d^3 r' d^3 r \end{aligned}$$

$$\begin{aligned} &= \frac{1}{\mathcal{V}} \int e^{i(-\vec{k}' + \vec{k} + \vec{q}) \cdot \vec{r}} d^3 r \\ &= \delta_{k+q, k'} \end{aligned}$$

$$\begin{aligned} \left\langle \psi_{k'} \middle| v e^{-i\vec{q} \cdot \vec{r}} \right| \psi_k \rangle &= \frac{1}{\mathcal{V}} \int \left\langle \psi(\vec{r}') \middle| e^{-i\vec{q} \cdot \vec{r}} \right| \psi(\vec{r}) \rangle e^{-i\vec{k}' \cdot \vec{r}'} e^{i\vec{k} \cdot \vec{r}} d^3 r' d^3 r \\ &= \frac{1}{\mathcal{V}} \int \delta(\vec{r}' - \vec{r}) e^{-i\vec{k}' \cdot \vec{r}'} e^{i\vec{k} \cdot \vec{r}} e^{-i\vec{q} \cdot \vec{r}} d^3 r' d^3 r \\ &= \frac{1}{\mathcal{V}} \int e^{i(-\vec{k}' + \vec{k} - \vec{q}) \cdot \vec{r}} d^3 r \\ &= \delta_{k-q, k'} \end{aligned}$$

$$c_{k'}^{(1)}(t) = \frac{iev}{\hbar} \int_{-\infty}^t \left[ \delta_{k+q, k'} e^{i(\omega_{k'k} - \omega - i\epsilon)t'} + \delta_{k-q, k'} e^{i(\omega_{k'k} + \omega - i\epsilon)t'} \right] dt'$$

The result is referred to as the random phase approximation (RPA).

(3) The perturbed state up to the first-order

$$\begin{aligned} |\Psi_k(t)\rangle &= e^{-i\omega_k t} |\psi_k\rangle + \frac{iev}{\hbar} \int_{-\infty}^t e^{i(\omega_{k+q,k} - \omega - i\epsilon)t'} dt' e^{-i\omega_{k+q} t} |\psi_{k+q}\rangle \\ &\quad + \frac{iev}{\hbar} \int_{-\infty}^t e^{i(\omega_{k-q,k} + \omega - i\epsilon)t'} dt' e^{-i\omega_{k-q} t} |\psi_{k-q}\rangle \end{aligned}$$

where

$$\begin{aligned}
\int_{-\infty}^t e^{i(\omega_{k+q,k} - \omega - i\epsilon)t'} dt' &= \frac{e^{i(\omega_{k+q,k} - \omega - i\epsilon)t}}{i(\omega_{k+q,k} - \omega - i\epsilon)} \\
&= \frac{i\hbar e^{i\omega_{k+q,k}t} e^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} \\
\int_{-\infty}^t e^{i(\omega_{k-q,k} + \omega - i\epsilon)t'} dt' &= \frac{e^{i(\omega_{k-q,k} + \omega - i\epsilon)t}}{i(\omega_{k-q,k} + \omega - i\epsilon)} \\
&= \frac{i\hbar e^{i\omega_{k-q,k}t} e^{i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon + i\hbar\epsilon}
\end{aligned}$$

Since

$$\begin{aligned}
e^{i\omega_{k+q,k}t} e^{-i\omega_{k+q}t} &= e^{i((\omega_{k+q} - \omega_k) - \omega_{k+q})t} = e^{-i\omega_k t} \\
e^{i\omega_{k-q,k}t} e^{-i\omega_{k-q}t} &= e^{i((\omega_{k-q} - \omega_k) - \omega_{k-q})t} = e^{-i\omega_k t} \\
|\Psi_k(t)\rangle &= e^{-i\omega_k t} |\psi_k\rangle - \frac{eve^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} e^{-i\omega_k t} |\psi_{k+q}\rangle \\
&\quad - \frac{eve^{i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon + i\hbar\epsilon} e^{-i\omega_k t} |\psi_{k-q}\rangle
\end{aligned}$$

Drop out the global phase  $e^{-i\omega_k t}$ .

$$|\Psi_k(t)\rangle = |\psi_k\rangle - \frac{eve^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} |\psi_{k+q}\rangle - \frac{eve^{i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon + i\hbar\epsilon} |\psi_{k-q}\rangle$$

(4) The electron density is

$$\rho(\vec{r}, t) = -e \sum_k \langle \Psi_k(t) | \Psi_k(t) \rangle = \rho_0 + \rho_{\text{ind}}(\vec{r}, t)$$

$$\text{Let } b_{k+q} = \frac{eve^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} \text{ and } b_{k-q} = \frac{eve^{i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon + i\hbar\epsilon}$$

$$|\Psi_k(t)\rangle = |\psi_k\rangle - b_{k+q} |\psi_{k+q}\rangle - b_{k-q} |\psi_{k-q}\rangle$$

$$\begin{aligned}
\langle \Psi_k(t) | \Psi_k(t) \rangle &= \left[ \langle \psi_k | \psi_k \rangle - b_{k+q} \langle \psi_k | \psi_{k+q} \rangle - b_{k+q}^* \langle \psi_{k+q} | \psi_k \rangle \right. \\
&\quad \left. - b_{k-q} \langle \psi_k | \psi_{k-q} \rangle - b_{k-q}^* \langle \psi_{k-q} | \psi_k \rangle + O(b^2) \right] \\
&= \frac{1}{V} \left[ 1 - b_{k+q} e^{i\vec{q} \cdot \vec{r}} - b_{k+q}^* e^{-i\vec{q} \cdot \vec{r}} - b_{k-q} e^{-i\vec{q} \cdot \vec{r}} - b_{k-q}^* e^{i\vec{q} \cdot \vec{r}} \right] \\
&= \frac{1}{V} \left[ 1 - (b_{k+q} + b_{k-q}^*) e^{i\vec{q} \cdot \vec{r}} - (b_{k+q}^* + b_{k-q}) e^{-i\vec{q} \cdot \vec{r}} \right]
\end{aligned}$$

Thus

$$-e \sum_k \frac{1}{V} \left[ 1 - (b_{k+q} + b_{k-q}^*) e^{i\vec{q} \cdot \vec{r}} - (b_{k+q}^* + b_{k-q}) e^{-i\vec{q} \cdot \vec{r}} \right] \\ = \rho_0 + \rho_{\text{ind}}(\vec{r}, t)$$

$$\Rightarrow \rho_{\text{ind}}(\vec{r}, t) = \frac{e}{V} \sum_k \left[ (b_{k+q} + b_{k-q}^*) e^{i\vec{q} \cdot \vec{r}} + (b_{k+q}^* + b_{k-q}) e^{-i\vec{q} \cdot \vec{r}} \right]$$

$$b_{k+q} + b_{k-q}^* = \frac{eve^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} + \frac{eve^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon - i\hbar\epsilon}$$

$$\rho_{\text{ind}}(\vec{r}, t) = \frac{e^2}{V} \sum_{k < k_F} \left[ \frac{ve^{i\vec{q} \cdot \vec{r}} e^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} + \frac{ve^{i\vec{q} \cdot \vec{r}} e^{-i\omega t} e^{\epsilon t}}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon - i\hbar\epsilon} + \text{c.c.} \right]$$

Since  $\sum_{k < k_F} = \sum_k f_0(\vec{k})$

$$\sum_{k < k_F} \left[ \frac{1}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} + \frac{1}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon - i\hbar\epsilon} \right]$$

$$= \sum_k \left[ \frac{f_0(\vec{k})}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} + \frac{f_0(\vec{k})}{\varepsilon_k - \varepsilon_{k-q} - \varepsilon - i\hbar\epsilon} \right]$$

$$= \sum_k \left[ \frac{f_0(\vec{k})}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} + \frac{f_0(\vec{k} + \vec{q})}{\varepsilon_{k+q} - \varepsilon_k - \varepsilon - i\hbar\epsilon} \right]$$

$$= \sum_k \left[ \frac{f_0(\vec{k})}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} - \frac{f_0(\vec{k} + \vec{q})}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} \right]$$

$$= \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon}$$

$$\rho_{\text{ind}}(\vec{r}, t) = \frac{e^2}{V} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\varepsilon_k - \varepsilon_{k+q} + \varepsilon + i\hbar\epsilon} ve^{i\vec{q} \cdot \vec{r}} e^{-i\omega t} e^{\epsilon t} + \text{c.c.}$$

- (5) Assume that the induced potential has the same wavelength and frequency response as the induced charge,

$$V_{\text{ind}}(\vec{r}, t) = \delta v e^{i\vec{q} \cdot \vec{r}} e^{-i\omega t} e^{\epsilon t} + \delta v e^{-i\vec{q} \cdot \vec{r}} e^{i\omega t} e^{\epsilon t}$$

The Poisson's equation

$$\nabla^2 V_{\text{ind}}(\vec{r}, t) = -\frac{\rho_{\text{ind}}(\vec{r}, t)}{\epsilon_0}$$

$$\Rightarrow q^2 \delta v = \frac{e^2}{\epsilon_0 \mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q} + \varepsilon + i\hbar\epsilon} v$$

$$\Rightarrow \delta v = \frac{e^2}{\epsilon_0 q^2} \frac{1}{\mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q} + \varepsilon + i\hbar\epsilon} v$$

$$v = v_{\text{ext}} + \delta v = v_{\text{ext}} + \frac{e^2}{\epsilon_0 q^2} \frac{1}{\mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q} + \varepsilon + i\hbar\epsilon} v$$

$$\Rightarrow v_{\text{ext}} = \left[ 1 - \frac{e^2}{\epsilon_0 q^2} \frac{1}{\mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q} + \varepsilon + i\hbar\epsilon} \right] v$$

The dielectric constant

$$\text{Let } \Pi(\vec{q}, \omega) = \frac{e^2}{\mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q} + \varepsilon + i\hbar\epsilon}$$

$$\epsilon(q, \omega) = 1 - \frac{\Pi(\vec{q}, \omega)}{\epsilon_0 q^2} = 1 - \frac{e^2}{\epsilon_0 q^2} \frac{1}{\mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q} + \varepsilon + i\hbar\epsilon}$$

## D. STATIC SCREENING

(1) If  $\omega \rightarrow 0$  and  $\vec{q}$  is small

$$\Pi(\vec{q}, 0) = \frac{e^2}{\mathcal{V}} \sum_k \frac{f_0(\vec{k}) - f_0(\vec{k} + \vec{q})}{\epsilon_k - \epsilon_{k+q}} = \frac{e^2}{(2\pi)^3} \int \frac{f_0(\vec{k} + \vec{q}) - f_0(\vec{k})}{\epsilon_{k+q} - \epsilon_k} d^3 k$$

$$f_0(\vec{k} + \vec{q}) - f_0(\vec{k}) \approx \frac{\partial f_0(\vec{k})}{\partial \varepsilon} \nabla \epsilon_k \cdot \vec{q} \approx \frac{\partial f_0(\vec{k})}{\partial \varepsilon} v_F \vec{k} \cdot \vec{q}$$

$$\epsilon_{k+q} - \epsilon_k \approx \nabla \epsilon_k \cdot \vec{q} \approx v_F \vec{k} \cdot \vec{q}$$

$$\Pi(\vec{q}, 0) = \frac{e^2}{(2\pi)^3} \int \frac{\frac{\partial f_0(\vec{k})}{\partial \varepsilon} v_F \vec{k} \cdot \vec{q}}{v_F \vec{k} \cdot \vec{q}} d^3 k$$

$$= \frac{e^2}{(2\pi)^3} \int \frac{\partial f_0(\vec{k})}{\partial \varepsilon} d^3 k$$

$$= e^2 \int \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} g(\varepsilon) d\varepsilon$$

where  $g(\varepsilon)$  is the density of single-particle states.

Since  $-\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} = \delta(\varepsilon - \varepsilon_F)$

$$\begin{aligned}\Pi(\vec{q}, 0) &= -e^2 \int \delta(\varepsilon - \varepsilon_F) g(\varepsilon) d\varepsilon \\ &= -e^2 g(\varepsilon_F) \\ &= -\frac{e^2}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} \\ &= -\frac{e^2 m k_F}{\pi^2 \hbar^2}\end{aligned}$$

$$\epsilon(q, 0) = 1 - \frac{\Pi(\vec{q}, 0)}{\epsilon_0 q^2} = 1 + \frac{e^2}{q^2} \frac{m k_F}{\pi^2 \hbar^2}$$

Define  $k_0^2 = \frac{me^2 k_F}{\pi^2 \hbar^2} = \frac{k_F}{(\pi^2 a_0)}$  ..... Thomas-Fermi wavevector

$$\epsilon(q, 0) = 1 + \frac{k_0^2}{q^2}$$

$$V(\vec{q}, 0) = \frac{e}{4\pi\epsilon_0} \frac{1}{q^2 + k_0^2} \xrightarrow{\text{Fourier transformation}} V(\vec{r}, 0) = \frac{e}{4\pi\epsilon_0} \frac{e^{-k_0 r}}{r}$$

(2) If  $\omega \rightarrow 0$  and  $\vec{q}$  is arbitrary

$$\begin{aligned}\Pi(\vec{q}, 0) &= \frac{e^2}{(2\pi)^3} \int \frac{f_0(\vec{k} + \vec{q}) - f_0(\vec{k})}{\varepsilon_{k+q} - \varepsilon_k} d^3 k \\ &= \frac{e^2}{(2\pi)^3} \int \left[ \frac{f_0(\vec{k})}{\varepsilon_k - \varepsilon_{k-q}} - \frac{f_0(\vec{k})}{\varepsilon_{k+q} - \varepsilon_k} \right] d^3 k \\ &= \frac{e^2}{(2\pi)^3} \int \left[ \frac{f_0(-\vec{k})}{\varepsilon_{-k} - \varepsilon_{-k-q}} - \frac{f_0(\vec{k})}{\varepsilon_{k+q} - \varepsilon_k} \right] d^3 k\end{aligned}$$

Since the electron energy is an even function of the wavevector.

$$\begin{aligned}\Pi(\vec{q}, 0) &= \frac{e^2}{(2\pi)^3} \int \left[ \frac{1}{\varepsilon_k - \varepsilon_{k+q}} - \frac{1}{\varepsilon_{k+q} - \varepsilon_k} \right] f_0(\vec{k}) d^3 k \\ &= \frac{e^2}{(2\pi)^3} \int \frac{2}{\varepsilon_k - \varepsilon_{k+q}} f_0(\vec{k}) d^3 k \\ &= \frac{e^2}{(2\pi)^3} \frac{2m}{\hbar^2} \int \frac{2}{-2\vec{k} \cdot \vec{q} - q^4} f_0(\vec{k}) d^3 k\end{aligned}$$

Assume  $T = 0 \Rightarrow f_0(\vec{k}) = \Theta(k - k_F)$

$$\begin{aligned}\Pi(\vec{q}, 0) &= -\frac{8\pi me^2}{(2\pi)^3 \hbar^2} \int_0^\infty \int_{-1}^1 \frac{\Theta(k - k_F)}{2kq \cos \theta + q^2} k^2 dk d(\cos \theta) \\ &= -\frac{8\pi me^2}{(2\pi)^3 \hbar^2 q} \int_0^{k_F} \frac{1}{2k} \ln \left| \frac{q + 2k}{q - 2k} \right| k^2 dk \\ &= -\frac{me^2 k_F}{8\pi^2 \hbar^2 q} \left[ 4q + 4k_F \left[ 1 - \left( \frac{q}{2k_F} \right)^2 \right] \ln \left| \frac{\frac{q}{2k_F} + 1}{\frac{q}{2k_F} - 1} \right| \right]\end{aligned}$$

Let  $x = \frac{q}{2k_F}$

$$\Pi(\vec{q}, 0) = -\frac{me^2 k_F}{\pi^2 \hbar^2} \left[ \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{x + 1}{x - 1} \right| \right] = -e^2 g(\varepsilon_F) F(x)$$

where  $F(x)$  is the Linhard dielectric function.

$$\epsilon(q, 0) = 1 - \frac{\Pi(\vec{q}, 0)}{\epsilon_0 q^2} = 1 + \frac{e^2}{\epsilon_0 q^2} g(\varepsilon_F) F(x)$$

There is a logarithmic singularity at  $q = \pm 2k_F$  because of the sharpness of the Fermi surface in  $k$ -space.

## E. PLASMONS

In the limit  $\omega \gg v_F q$ , examine the case where  $T = 0$

$$\Pi(\vec{q}, \omega) = \frac{e^2}{\mathcal{V}} \sum_k \frac{\varepsilon_{k+q} - \varepsilon_k}{(\varepsilon + i\hbar\omega)^2 - (\varepsilon_k - \varepsilon_{k+q})^2}$$

$$\text{Since } \varepsilon_{k+q} - \varepsilon_k = \frac{\hbar^2}{2m} (\vec{q}^2 + 2\vec{k} \cdot \vec{q})$$

$$\Pi(\vec{q}, \omega) = \frac{1}{2m} \frac{e^2}{\mathcal{V}} \sum_k \frac{\vec{q}^2 + 2\vec{k} \cdot \vec{q}}{\omega^2}$$

For every  $\vec{k}$ , there will be a corresponding contribution from  $-\vec{k}$ .

$$\sum_k \vec{k} \cdot \vec{q} = 0$$

$$\Rightarrow \Pi(\vec{q}, \omega) = \frac{1}{2m} \frac{e^2}{\mathcal{V}} 2 \sum_k \frac{\vec{q}^2}{\omega^2} = \frac{1}{2m} \frac{e^2}{\mathcal{V}} \frac{\vec{q}^2}{\omega^2} 2N = \frac{n\vec{q}^2}{m\omega^2}$$

The dielectric function becomes

$$\epsilon(q, \omega) = 1 - \frac{\Pi(\vec{q}, \omega)}{\epsilon_0 q^2} = 1 - \frac{e^2}{\epsilon_0 m\omega^2} \frac{n}{m\omega^2} \equiv 1 - \frac{\omega_p^2}{\omega^2}$$

As  $\omega = \omega_p$ ,  $\epsilon(q, \omega) = 0$  and  $V_{\text{tot}}(\vec{q}, \omega)$  diverges.

⇒ The physical meaning of this divergence is that an external perturbation at this energy will give rise to a self-sustaining oscillation, also known as a plasmon.

## F. FRIEDEL OSCILLATIONS

Consider a spherically symmetric potential

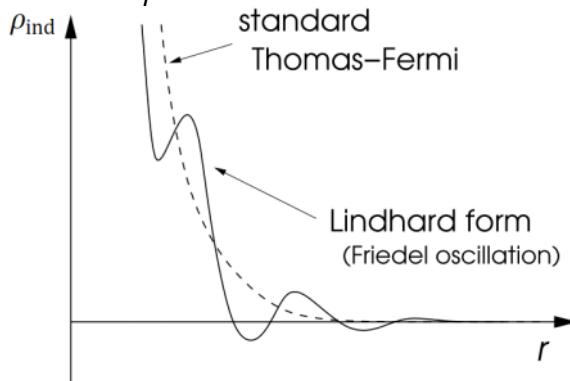
$$\psi_{k,\ell} \sim \frac{1}{r} \sin\left(kr - \frac{1}{2}\ell\pi + \eta_\ell\right) P_\ell(\cos\theta)$$

The electron density associated with phase-shifted waves is

$$\begin{aligned}\rho_{\text{ind}} &= e^2 \sum_l 2(2l+1) \int_0^{k_F} \left\{ |\psi_{k,l}(\eta_l)|^2 - |\psi_{k,l}(0)|^2 \right\} \frac{dk}{\pi R} \\ &= \frac{2e^2}{2\pi^2} \sum_l (2l+1) \int_0^{k_F} \left\{ \sin^2\left(kr - \frac{1}{2}\ell\pi + \eta_\ell\right) - \sin^2\left(kr - \frac{1}{2}\ell\pi\right) \right\} \frac{dk}{r^2} \\ &= \frac{2e^2}{2\pi^2} \sum_l (2l+1) \int_0^{k_F} \sin(2kr - \ell\pi + \eta_\ell) \sin(\eta_\ell) \frac{d(kr)}{r^3} \\ &= \frac{2e^2}{2\pi^2} \sum_l (2l+1) (-1)^l \sin(\eta_\ell) \frac{\cos(2k_F r + \eta_\ell)}{r^3}\end{aligned}$$

As  $r \rightarrow \infty$

$$\rho_{\text{ind}} \sim \frac{\cos(2k_F r)}{r^3}$$



# 8-4 Landau Fermi Liquid Theory

Friday, August 09, 2013 10:08 AM

OS:

We can study metals as a free electron gas, and indeed it gives (roughly) the correct physical quantities. However, there are two problems with this picture. First, the electrons are contained in a lattice. Bloch's theorem tells us that free electrons in a lattice behave as if they are in homogeneous space, except for some amplitudes. Therefore let's ignore the lattice (and the phonons too) for simplicity, the so called jellium model. We now have to explain the second problem, namely that the electron-electron coulomb interaction will not change radically the free electron conclusions. This is what Fermi's liquid theory is for.

## A. LIFE-TIME OF SINGLE-PARTICLE EXCITATIONS

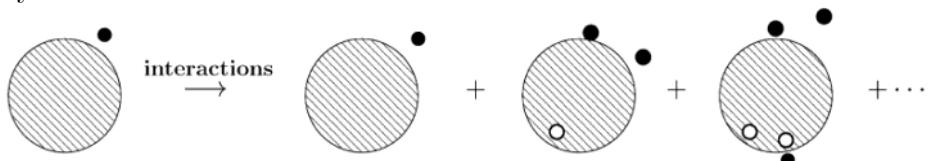
### (1) Ground state (Gell-Mann & Low theorem 1951)

The ground state of an interacting theory can be related to the ground state of the corresponding non-interacting theory with adiabatically switching on the interactions.

⇒ As the interactions are slowly turned on, the non-interacting states are assumed to smoothly and continuously evolve into interacting states, and that this evolution takes place without hitting any singular behavior. Such a singularity would signal an instability of the ground state and should be viewed as a phase transition. Thus, if there are no phase transitions, there should be a smooth connection between non-interacting and interacting states.

### (2) Excitation (Landau 1957)

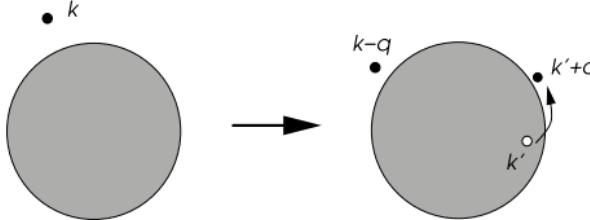
Add one electron with momentum  $\vec{k}$  to ground state of the interacting system at  $T = 0$ .



The additional electron can not scatter into an occupied momentum state below the Fermi surface. The decay of the electron state above the Fermi energy happens through scattering by creating particle-hole excitations. Therefore, it changes its momentum from  $\vec{k}$  to  $\vec{k} - \vec{q}$ , and then a hole appears at  $\vec{k}'$  and a second electron with wavevector  $\vec{k}' + \vec{q}$  is created outside the Fermi surface. All of them should satisfy the conservation of energy and momentum, i.e.,

$$\vec{k} = (\vec{k} - \vec{q}) + (\vec{k}' + \vec{q}) - \vec{k}'$$

$$\varepsilon_k = \varepsilon_{k-q} - (\varepsilon_{k'} - \varepsilon_{k'+q}) \Rightarrow \varepsilon_{k'+q} - \varepsilon_{k'} = \varepsilon_k - \varepsilon_{k-q}$$



The lifetime  $\tau_k$

$$\frac{1}{\tau_k} = \frac{2\pi}{\hbar} \frac{1}{V^2} \sum_{k', q} \left| \langle \vec{k} | \hat{V}_q | \vec{k} - \vec{q}, \vec{k}' + \vec{q}, \vec{k}' \rangle \right|^2 f_{k'} (1 - f_{k'+q}) (1 - f_{k-q}) \times \delta ((\varepsilon_{k'+q} - \varepsilon_{k'}) - (\varepsilon_k - \varepsilon_{k-q}))$$

where  $\varepsilon_{k'+q} - \varepsilon_{k'}$  is the energy spectrum for individual electron-hole pairs and  $\varepsilon_k - \varepsilon_{k-q}$  is the energy loss of the decaying electron.

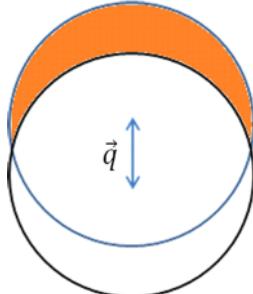
**OS:**

The Fermi function guarantee that the state  $\vec{k}'$  is indeed occupied by an electron, while the final states  $\vec{k}' + \vec{q}$  and  $\vec{k} - \vec{q}$  are empty and therefore available for occupation after the scattering event.

Let  $\hbar\omega_{k'q} = \varepsilon_{k'+q} - \varepsilon_{k'}$  and  $\hbar\omega_{kq} = \varepsilon_k - \varepsilon_{k-q}$

We first take the integral over  $k'$ ,

$$\begin{aligned}
S(q) &= \frac{1}{V} \sum_{k'} f_{k'} (1 - f_{k'+q}) \delta(\hbar\omega_{k'q} - \hbar\omega_{kq}) \\
&= \frac{1}{V} \sum_{\substack{|k'| < k_F \\ |k'+q| > k_F}} \delta(\hbar\omega_{k'q} - \hbar\omega_{kq}) \\
&= \frac{1}{(2\pi)^3} \int_{\substack{|k'| < k_F \\ |k'+q| > k_F}} \delta(\hbar\omega_{k'q} - \hbar\omega_{kq}) d^3 k'
\end{aligned}$$



The shaded area is the region in which  $|k'| < k_F$  and  $|k' + q| > k_F$ .  
OS:

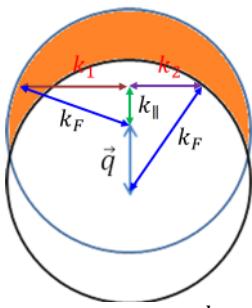
The momenta included by the region defined by  $|\vec{k}'| < k_F$  and  $|\vec{k}' + \vec{q}| > k_F$ , which is the crescent above the lower sphere. The shaded region (orange color) is found by overlaying two fermi spheres and displacing one sphere by  $-\vec{q}$ .

The integration is carried out in cylindrical coordinates and we choose  $\hat{z}$  to lie along  $\vec{q}$ . For a given energy  $\hbar\omega_{kq}$ , the longitudinal component  $k'_\parallel = \vec{k}' \cdot \hat{z}$  is fixed by energy conservation:

$$\hbar\omega_{kq} = \hbar\omega_{k'q} = \frac{\hbar^2}{2m} (2k'_\parallel q + q^2)$$

For a given  $k'_\parallel$ , the upper and lower boundaries in the radial direction are

$$k_1^2 = k_F^2 - k'^2_\parallel, \quad k_2^2 = k_F^2 - (\vec{k}' + \vec{q})^2, \quad k_1 > k_2$$



$$\begin{aligned}
 S(q) &= \frac{1}{(2\pi)^3} \int_{k_2}^{k_1} k'_\perp dk'_\perp \int_0^{2\pi} d\theta \int_0^{k_F} \delta(\hbar\omega_{k'q} - \hbar\omega_{kq}) dk'_\parallel \\
 &= \frac{1}{(2\pi)^2} \int_{k_2}^{k_1} k'_\perp dk'_\perp \int_0^{k_F} \delta\left(\frac{\hbar^2 q k'_\parallel}{m} + \frac{\hbar^2 q^2}{2m} - \hbar\omega_{kq}\right) dk'_\parallel \\
 &= \frac{1}{(2\pi)^2} \frac{1}{2} (k_1^2 - k_2^2) \frac{m}{\hbar^2 q}
 \end{aligned}$$

$$k_1^2 - k_2^2 = (\vec{k}'_\parallel + \vec{q})^2 - k'^2_\parallel = \frac{2m\omega_{kq}}{\hbar}$$

$$g(\varepsilon_F) = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} \Bigg|_{E_F = \hbar^2 k_F^2 / 2m} = \frac{mk_F}{\pi^2 \hbar^2}$$

$$S(q) = \frac{1}{4\pi^2} \frac{m}{\hbar^2 q} \frac{m\omega_{kq}}{\hbar} = \frac{g(\varepsilon_F)}{4qk_F} \frac{m\omega_{kq}}{\hbar} = \frac{g(\varepsilon_F)}{4v_F} \frac{\omega_{kq}}{q}$$

$$\begin{aligned}
 \frac{1}{\tau_k} &= \frac{2\pi}{\hbar} \frac{2}{V} \sum_q |V_q|^2 \frac{g(\varepsilon_F)}{4v_F} \frac{\omega_{kq}}{q} (1 - f_{k-q}) \\
 &= \frac{g(\varepsilon_F)}{(2\pi)^2 2\hbar v_F} \int_{|k-q| > k_F} |V_q|^2 \frac{\omega_{kq}}{q} d^3q
 \end{aligned}$$

$$\hbar\omega_{kq} = \varepsilon_k - \varepsilon_{k-q} = \frac{\hbar^2}{2m} (2\vec{k} \cdot \vec{q} - q^2) = \frac{\hbar^2}{2m} (2kq \cos \theta - q^2)$$

Since  $\hbar\omega_{kq} > 0 \Rightarrow k^2 \geq (\vec{k} - \vec{q})^2 \geq k_F^2$

$$1. \quad (\vec{k} - \vec{q})^2 \geq k_F^2$$

$$k^2 - 2kq \cos \theta + q^2 \geq k_F^2 \Rightarrow \cos \theta_2 = \frac{k^2 - k_F^2 + q^2}{2kq}$$

$$2. \quad k^2 \geq (\vec{k} - \vec{q})^2$$

$$k^2 \geq k^2 - 2kq \cos \theta + q^2 \Rightarrow \cos \theta_1 = \frac{q}{2k}$$

$$\begin{aligned}
\frac{1}{\tau_k} &= \frac{g(\varepsilon_F)}{(2\pi)4mv_F} \int |V_q|^2 q^2 dq \int_{\cos \theta_2}^{\cos \theta_1} (2k \cos \theta - q) d(\cos \theta) \\
&= \frac{g(\varepsilon_F)}{(2\pi)4mv_F} \int |V_q|^2 q^2 dq \left[ \frac{1}{4k} (2k \cos \theta - q)^2 \right]_{\cos \theta_2}^{\cos \theta_1} \\
&= \frac{g(\varepsilon_F)}{(2\pi)4mv_F} \int |V_q|^2 dq \frac{1}{4k} (k^2 - k_F^2)^2 \\
&= \frac{1}{8\pi} \frac{g(\varepsilon_F)}{v_F} \frac{m}{\hbar^4 k} (\varepsilon_k - \varepsilon_F)^2 \int |V_q|^2 dq
\end{aligned}$$

We assume that the potential is short-ranged potential due to screening and by approximation  $1/k \approx 1/k_F$

$$\frac{1}{\tau_k} \propto (\varepsilon_k - \varepsilon_F)^2 \Rightarrow \tau_k \propto \frac{1}{(\varepsilon_k - \varepsilon_F)^2}$$

The life-time of an added electron above the Fermi surface diverges as  $\varepsilon_k \rightarrow \varepsilon_F$ . We can think of the extra electron as a well-defined **quasiparticle** with a large life-time for  $\varepsilon_k$  close to  $\varepsilon_F$  which is dressed by particle-hole excitations but keeps it particle-like character.

OS:

Quasiparticle doesn't mean "not really a particle", it means "more than just a particle".

## B. EMERGENT QUASIPARTICLE AND ADIABATIC CONTINUITY

### (1) Adiabatic continuity

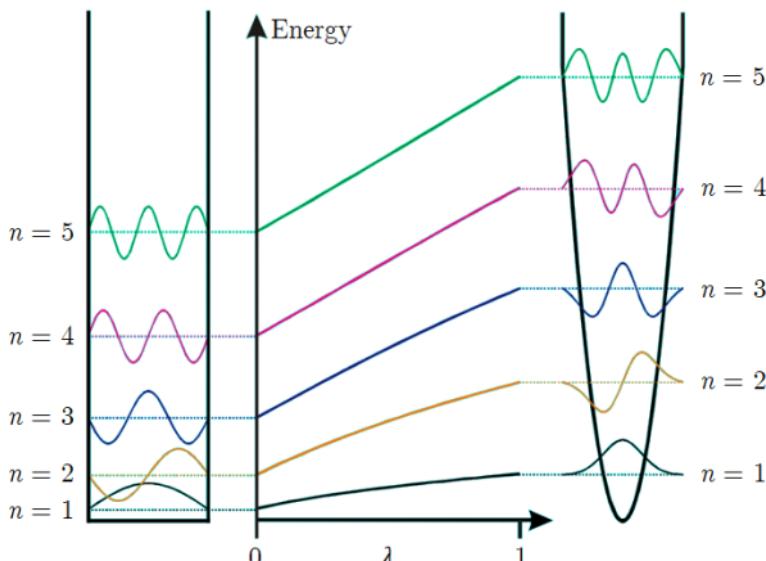
As one gradually turns on the interactions the excited states of the system smoothly evolve from those in the noninteracting system. As a result the quasiparticles have the same quantum numbers and statistics as the constituent particles.

EXAMPLES:

Consider a particle confined in an infinite potential well,

$$-\frac{1}{2} \frac{d^2 \psi}{dx^2} + V(x) \psi = \varepsilon \psi, \quad V(x) = \begin{cases} \frac{1}{2} \lambda x^2, & |x| < L \\ \infty, & |x| \geq L \end{cases}$$

As  $\lambda = 0$ , the eigenfunctions  $\psi_n$  can be labelled by the integer number  $n = 1, 2, 3, \dots$



As  $\lambda \neq 0$  (switch on the weak quadratic potential), the new eigenstates of the problem involve a mixing of all the eigenstates of the original unperturbed problem.

However the quantum number still remains a good way of labelling the eigenstates of the more complicated problem.

## (2) Adiabatic discontinuity.

The quasiparticles do NOT have the same quantum numbers and statistics as the constituent particles.

### EXAMPLES:

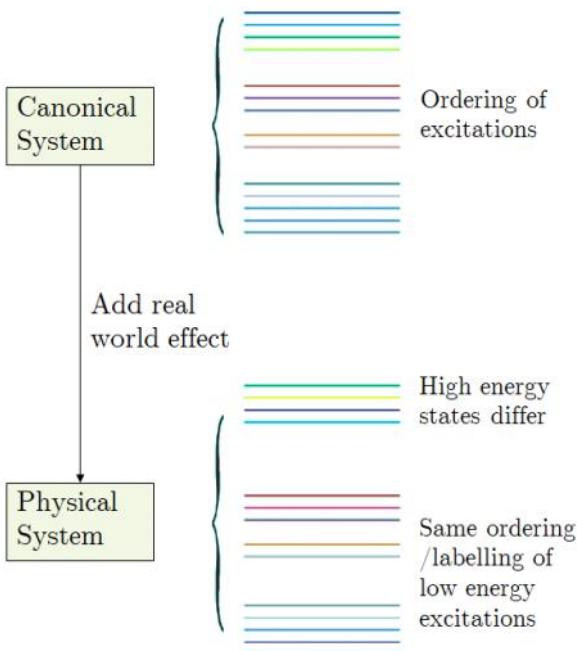
Spin wave in a spin- $1/2$  Heisenberg antiferromagnet:

The magnons have spin one and act like bosons. In contrast, the constituent particles are localized electron that are fermions with spin- $1/2$ .

## C. PHENOMENOLOGICAL THEORY OF FERMI LIQUIDS

### (1) Adiabatic continuity:

As turns on the interactions between electrons slowly, there is a one-to-one mapping of the low energy eigenstates of the interacting electrons with those of the non-interacting Fermi gas.



The weakly excited states of a Fermi liquid greatly resemble those of a weakly excited Fermi gas. These states can be described with a set of elementary excitations with spin- $1/2$  and momenta close to the Fermi surface.

### OS:

These labels are not to be associated with electrons but to 'quasiparticles' to remind us that the states and energies are different from the corresponding electron in the non-interacting problem.

- (2) Since each quasiparticle contributes additively to the total entropy of the system, the quasiparticle distribution function is unchanged from the free particle result.

### PROOF:

Since the entropy depends only on quantum numbers  $k$ ,

$$S = -k_B \sum_{k\sigma} [n_{k\sigma} \ln n_{k\sigma} + (1 - n_{k\sigma}) \ln(1 - n_{k\sigma})]$$

Maximize the entropy subject to a fixed energy and particle number

$$\Rightarrow n_{k\sigma} = \frac{1}{e^{(\tilde{\varepsilon}_{k\sigma} - \mu)/k_B T} + 1}$$

where  $\tilde{\varepsilon}_{k\sigma}$  is the effective quasiparticle dispersion.

■

- (3) In an interacting system, unlike the free Fermi gas, the energy of individual excitations will not generally add to yield the total system energy. Landau accounted for the modified energy through two terms:

1. First, when a quasiparticle moves there will now be a back-flow in the filled Fermi sea as the quasiparticle 'pushes' the ground state out of the way. This modies the inertial mass of the quasiparticle  $m \rightarrow m^*$ .

**OS:**

Note that this is in addition to the effect of the crystal lattice which produces a band mass which can be included in the free electron picture and also the change induced by interactions with phonons.

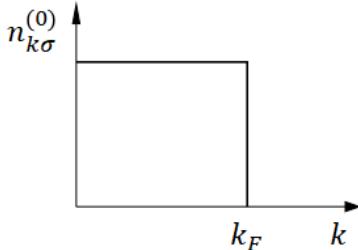
2. Second, a quasiparticle's energy also depends on the distribution of other quasiparticles.

- (4) The total energy of the interacting system is expanded as a functional of the quasiparticle distribution  $\delta n_{k\sigma}$

$$\delta n_{k\sigma} = n_{k\sigma} - n_{k\sigma}^{(0)}$$

where

$$n_{k\sigma}^{(0)} = \Theta(k_F - |\vec{k}|)$$



implies a solid Fermi surface.

The phenomenological energy functional is

$$E = E_0 + \sum_{k\sigma} \varepsilon_{k\sigma} \delta n_{k\sigma} + \frac{1}{2\mathcal{V}} \sum_{k,k'} \sum_{\sigma\sigma'} f_{\sigma,\sigma'}(\vec{k}, \vec{k}') \delta n_{k\sigma} \delta n_{k'\sigma'}$$

$$= E_0 + \sum_{k\sigma} \left[ \varepsilon_{k\sigma} + \frac{1}{2\mathcal{V}} \sum_{k'\sigma'} f_{\sigma,\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \right] \delta n_{k\sigma}$$

The phenomenological parameters  $\varepsilon_{k\sigma}$  and  $f_{\sigma,\sigma'}(\vec{k}, \vec{k}')$  have to be determined by experiments or by means of a microscopic theory.

The variational derivative gives the effective quasiparticle dispersion,

$$\tilde{\varepsilon}_{k\sigma} = \frac{\delta E}{\delta n_{k\sigma}} = \varepsilon_{k\sigma} + \frac{1}{\mathcal{V}} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'}$$

The second variational derivative gives the coupling between the quasiparticles,

$$\frac{\delta E}{\delta n_{k\sigma} \delta n_{k'\sigma'}} = \frac{1}{\mathcal{V}} f_{\sigma\sigma'}(\vec{k}, \vec{k}')$$

- (5) For an isotropic system, consider only quasiparticles in the vicinity of the Fermi surface where  $|\vec{k}|, |\vec{k}'| \approx k_F$

$$f_{\sigma\sigma'}(\vec{k}, \vec{k}') = f^s(\hat{k}, \hat{k}') + \sigma\sigma' f^a(\hat{k}, \hat{k}'), \quad \hat{k} = \frac{\vec{k}}{|\vec{k}|}$$

The symmetric  $f^s(\hat{k}, \hat{k}')$  and antisymmetric  $f^a(\hat{k}, \hat{k}')$  can be expanded in Legendre-polynomials

$$f^{s,a}(\hat{k}, \hat{k}') = \sum_{l=0}^{\infty} f_l^{s,a} P_l(\cos \theta_{\hat{k}, \hat{k}'})$$

OS:

$$\frac{1}{4\pi} \int P_l(\cos \theta_k) P_{l'}(\cos \theta_k) d\Omega_k = \frac{\delta_{ll'}}{2l+1}$$

The bare quasiparticle dispersion

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

The Fermi velocity

$$\vec{v}_F = \frac{1}{\hbar} \nabla_k \varepsilon_k \Big|_{k_F} = \frac{\hbar \vec{k}_F}{m^*}$$

The Fermi volume is conserved

$$k_F = (3\pi^2 n)^{1/3}$$

The density of states at Fermi energy

$$g(\varepsilon_F) = \frac{1}{V} \sum_{k\sigma} \delta(\varepsilon_F - \varepsilon_{k\sigma}) = \frac{m^* k_F}{\pi^2 \hbar^2}$$

Define Landau parameters:

$$F_l^S = g(\varepsilon_F) f_l^S$$

$$F_l^a = g(\varepsilon_F) f_l^a$$

## D. EXPERIMENTALLY DETERMINING LANDAU PARAMETERS

### (1) Specific heat

The entropy for the quasiparticles is

$$S = -k_B \sum_{k\sigma} [n_{k\sigma} \ln n_{k\sigma} + (1 - n_{k\sigma}) \ln(1 - n_{k\sigma})]$$

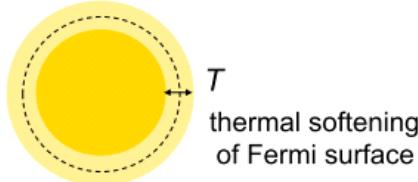
where

$$n_{k\sigma} = \frac{1}{e^{(\tilde{\varepsilon}_{k\sigma} - \mu)/k_B T} + 1} \text{ and } \tilde{\varepsilon}_{k\sigma} = \varepsilon_{k\sigma} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'}$$

Since there are as many particles and holes, they cancel in the correction term, i.e.,

$$\frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} = 0 \Rightarrow \tilde{\varepsilon}_{k\sigma} = \varepsilon_{k\sigma}$$

$$\Rightarrow n_{k\sigma} = \frac{1}{e^{\xi_k/k_B T} + 1}, \quad \xi_k = \varepsilon_{k\sigma} - \varepsilon_F$$



implies a *thermal softening of the Fermi surface*.

The specific heat is

$$\begin{aligned} C(T) &= \frac{1}{V} T \frac{\partial S}{\partial T} \\ &= -\frac{k_B T}{V} \sum_{k\sigma} \frac{e^{\xi_k/k_B T}}{(e^{\xi_k/k_B T} + 1)^2} \frac{\xi_k}{k_B T^2} \ln \frac{n_{k\sigma}}{1 - n_{k\sigma}} \\ &= -\frac{k_B T}{V} \sum_{k\sigma} \frac{1}{4 \cosh(\xi_k/2k_B T)^2} \frac{\xi_k}{k_B T^2} \frac{\xi_k}{k_B T} \end{aligned}$$

In the limit  $T \rightarrow 0$

$$\begin{aligned}
\frac{C(T)}{T} &\approx \frac{g(\varepsilon_F)}{4k_B T^3} \int \frac{\xi^2}{\cosh^2(\xi/2k_B T)} d\xi \\
&\approx \frac{g(\varepsilon_F) k_B^2}{4} \int_{-\infty}^{\infty} \frac{x^2}{\cosh^2(x/2)} dx \\
&= \frac{\pi^2 g(\varepsilon_F) k_B^2}{3} \\
\Rightarrow C(T) &= \gamma T, \quad \gamma = \frac{\pi^2 g(\varepsilon_F) k_B^2}{3} = \frac{\pi^2 m^* k_F}{3 \pi^2 \hbar^2} k_B^2 = \frac{m^* k_F}{3 \hbar^2} k_B^2
\end{aligned}$$

The effective mass  $m^*$  of the quasiparticles can directly determined by measuring the specific heat of the system.

## (2) Compressibility

A Fermi gas has a finite compressibility because each fermion occupies a finite amount of space due to the Pauli principle. The compressibility is defined as

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,N}$$

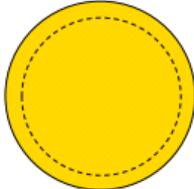
where  $p$  is the uniform hydrostatic pressure.

The shift of the quasiparticle energies in the presence of a uniform pressure  $p$ ,

$$\delta \varepsilon_k = \frac{\partial \varepsilon_k}{\partial p} \delta p = \frac{\partial \varepsilon_k}{\partial \vec{k}} \cdot \frac{\partial \vec{k}}{\partial V} \frac{\partial V}{\partial p} \delta p = \frac{\kappa^{(0)}}{3} \hbar \vec{v}_k \cdot \vec{k} \delta p = \gamma_k \kappa^{(0)} \delta p$$

with

$$\gamma_k = \hbar \vec{v}_k \cdot \frac{\vec{k}}{3} = \frac{2 \varepsilon_{k\sigma}}{3}$$



change of  
Fermi volume

Analogous, the shift of the renormalized quasiparticle energies,

$$\begin{aligned}
\delta \tilde{\varepsilon}_{k\sigma} &= \gamma_k \kappa^{(0)} \delta p + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \\
&= \gamma_k \kappa^{(0)} \delta p + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \frac{\partial n_{k'\sigma'}}{\partial \tilde{\varepsilon}_{k'\sigma'}} \delta \tilde{\varepsilon}_{k'\sigma'} \\
&= \gamma_k \kappa^{(0)} \delta p - \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta (\tilde{\varepsilon}_{k'\sigma'} - \varepsilon_F) \gamma_{k'} \kappa \delta p \\
&= \gamma_k \kappa \delta p
\end{aligned}$$

At the Fermi surface  $\gamma_k = 2\varepsilon_F/3$

$$\begin{aligned}
\delta \tilde{\varepsilon}_{k\sigma} &= \gamma_k \kappa^{(0)} \delta p - \gamma_k \frac{1}{V} \sum_{k'\sigma'} f^s(\hat{k}, \hat{k}') \delta (\tilde{\varepsilon}_{k'\sigma'} - \varepsilon_F) \kappa \delta p = \gamma_k \kappa \delta p \\
\Rightarrow \kappa &= \kappa^{(0)} - \kappa \frac{1}{V} \sum_{k'\sigma'} f^s(\hat{k}, \hat{k}') \delta (\tilde{\varepsilon}_{k'\sigma'} - \varepsilon_F) \\
&= \kappa^{(0)} - \kappa g(\varepsilon_F) \int f^s(\hat{k}, \hat{k}') \frac{d\Omega_{\hat{k}'}}{4\pi} \\
&= \kappa^{(0)} - \kappa F_0^s \\
\Rightarrow \kappa &= \frac{\kappa^{(0)}}{1 + F_0^s}
\end{aligned}$$

Since

$$\begin{aligned}
\frac{1}{\kappa^{(0)}} &= -V \frac{\partial p}{\partial V} \text{ and } p = -\left(\frac{\partial E^{(0)}}{\partial V}\right) \\
E^{(0)} &= \sum_{k\sigma} \varepsilon_{k\sigma} = \frac{3}{5} N \varepsilon_F = \frac{3}{5} N \frac{\hbar^2 k_F^2}{2m^*} = \frac{3}{10} \frac{\hbar^2 N}{m^*} (3\pi^2 n)^{2/3} \\
\Rightarrow p &= \frac{1}{5} \frac{\hbar^2 N}{m^*} (3\pi^2 n)^{2/3} \frac{1}{V} \\
\Rightarrow \frac{1}{\kappa^{(0)}} &= \frac{1}{3} \frac{\hbar^2 N}{m^*} (3\pi^2 n)^{2/3} \frac{1}{V} = \frac{2}{3} n \varepsilon_F \\
\Rightarrow \kappa &= \frac{3}{2n\varepsilon_F} \frac{1}{1 + F_0^s} = \frac{1}{n^2} \frac{g(\varepsilon_F)}{1 + F_0^s}
\end{aligned}$$

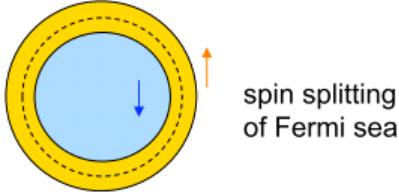
### (3) Spin susceptibility

In a magnetic field  $H$  coupling to the electron spins the bare quasiparticle energy is supplemented by the Zeeman term,

$$\varepsilon_{k\sigma} = \frac{\hbar^2 k^2}{2m^*} - g\mu_B H \frac{\sigma}{2}$$

The shift of the quasiparticle energy due to the applied field is

$$\delta\varepsilon_{k\sigma} = \varepsilon_{k\sigma}(H) - \varepsilon_{k\sigma}(0) = -g\mu_B H \frac{\sigma}{2}$$



Analogous, the shift of the renormalized quasiparticle energy is

$$\delta\tilde{\varepsilon}_{k\sigma} = \tilde{\varepsilon}_{k\sigma}(H) - \tilde{\varepsilon}_{k\sigma}(0)$$

$$\begin{aligned} &= -g\mu_B H \frac{\sigma}{2} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \\ &= -g\mu_B H \frac{\sigma}{2} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \frac{\partial n_{k'\sigma'}}{\partial \tilde{\varepsilon}_{k'\sigma'}} \delta \tilde{\varepsilon}_{k'\sigma'} \\ &= -g\mu_B H \frac{\sigma}{2} - \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta(\tilde{\varepsilon}_{k'\sigma'} - \varepsilon_F) \left( -\tilde{g}\mu_B H \frac{\sigma'}{2} \right) \\ &= -\tilde{g}\mu_B H \frac{\sigma}{2} \\ \Rightarrow \tilde{g} &= g - \tilde{g} \frac{1}{V} \sum_{k'\sigma'} f^a(\hat{k}, \hat{k}') \delta(\tilde{\varepsilon}_{k'\sigma'} - \varepsilon_F) \\ &= g - \tilde{g} \int f^a(\hat{k}, \hat{k}') \frac{d\Omega_{\hat{k}'}}{4\pi} \\ &= g - \tilde{g} F_0^a \\ \Rightarrow \tilde{g} &= \frac{g}{1 + F_0^a} \end{aligned}$$

The magnetization of the system is

$$\begin{aligned} M &= g\mu_B \sum_{k\sigma} \delta n_{k\sigma} \frac{\sigma}{2} \\ &= g\mu_B \sum_{k\sigma} \frac{\partial n_{k\sigma}}{\partial \tilde{\varepsilon}_{k\sigma}} \delta \tilde{\varepsilon}_{k\sigma} \frac{\sigma}{2} \\ &= -g\mu_B \sum_{k\sigma} \delta(\tilde{\varepsilon}_{k\sigma} - \varepsilon_F) \frac{\sigma}{2} \left( -\tilde{g}\mu_B \frac{\sigma}{2} \right) H \\ &= \frac{g^2 \mu_B^2}{1 + F_0^a} V g(\varepsilon_F) \frac{\sigma^2}{4} H \\ &= V \frac{\mu_B^2 g(\varepsilon_F)}{1 + F_0^a} H \end{aligned}$$

The susceptibility is

$$\chi = \frac{1}{\mathcal{V} H} = \frac{\mu_B^2 g(\varepsilon_F)}{1 + F_0^a}$$

For the magnetic susceptibility, the Landau parameter  $F_0^a$  and the effective mass  $m^*$  (through  $g(\varepsilon_F)$ ) lead to a renormalization compared to the free electron susceptibility.

#### (4) Quasiparticle current

The current density of quasiparticles is

$$j_q = \frac{1}{\mathcal{V}} \sum_{k\sigma} v_k n_{k\sigma}$$

where

$$\begin{aligned} v_k &= \frac{1}{\hbar} \nabla_k \tilde{\varepsilon}_{k\sigma} = \frac{1}{\hbar} \left( \nabla_k \varepsilon_{k\sigma} + \frac{1}{\mathcal{V}} \sum_{k'\sigma'} \nabla_k f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \right) \\ j_q &= \frac{1}{\mathcal{V}} \sum_{k\sigma} \left( \frac{1}{\hbar} \nabla_k \varepsilon_{k\sigma} + \frac{1}{\mathcal{V}} \sum_{k'\sigma'} \frac{1}{\hbar} \nabla_k f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \right) n_{k\sigma} \\ &= \frac{1}{\mathcal{V}} \sum_{k\sigma} \frac{1}{\hbar} \nabla_k \varepsilon_{k\sigma} n_{k\sigma} + \frac{1}{\mathcal{V}^2} \sum_{k\sigma} \sum_{k'\sigma'} \left[ \frac{1}{\hbar} \nabla_k f_{\sigma\sigma'}(\vec{k}, \vec{k}') \right] \delta n_{k'\sigma'} n_{k\sigma} \\ &= \frac{1}{\mathcal{V}} \sum_{k\sigma} \frac{\hbar \vec{k}}{m^*} n_{k\sigma} - \frac{1}{\mathcal{V}^2} \sum_{k\sigma} \sum_{k'\sigma'} \left[ \frac{1}{\hbar} \nabla_k n_{k\sigma} \right] f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \end{aligned}$$

Since  $n_{k\sigma} = n_{k\sigma}^{(0)} + \delta n_{k\sigma}$

$$j_q = \frac{1}{\mathcal{V}} \sum_{k\sigma} \frac{\hbar \vec{k}}{m^*} \delta n_{k\sigma} - \frac{1}{\mathcal{V}^2} \sum_{k\sigma} \sum_{k'\sigma'} \left[ \frac{1}{\hbar} \nabla_k n_{k\sigma}^{(0)} \right] f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} + O(q^2)$$

$$\nabla_k n_{k\sigma}^{(0)} = \frac{\partial n_{k\sigma}^{(0)}}{\partial \varepsilon_{k\sigma}} \nabla_k \varepsilon_{k\sigma} = -\delta(\varepsilon_{k\sigma} - \varepsilon_F) \nabla_k \varepsilon_{k\sigma} = -\delta(\varepsilon_{k\sigma} - \varepsilon_F) \frac{\hbar^2 \vec{k}}{m^*}$$

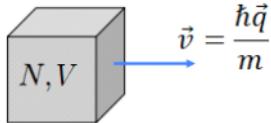
$$f_{\sigma'\sigma}(\vec{k}', \vec{k}) = f_{\sigma\sigma'}(\vec{k}, \vec{k}')$$

$$j_q = \frac{1}{\mathcal{V}} \sum_{k\sigma} \frac{\hbar \vec{k}}{m^*} \delta n_{k\sigma} + \frac{1}{\mathcal{V}^2} \sum_{k\sigma} \sum_{k'\sigma'} \delta(\varepsilon_{k'\sigma'} - \varepsilon_F) \frac{\hbar \vec{k}'}{m^*} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k\sigma}$$

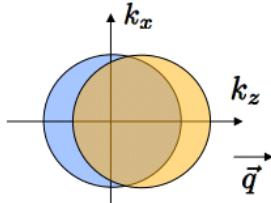
The first term of equation denotes quasiparticle current, while the second term can be interpreted as a drag current, an induced motion (backflow) of the other particles due to interactions.

From a different viewpoint, consider the system as being in the inertial

frame with a velocity  $\hbar\vec{q}/m$ , as the momenta of all particles are shifted by  $\vec{q}$ .



The Fermi surface is shifted



shifted Fermi sea  
 $n_{k\sigma} \approx n_{k+q,\sigma}^{(0)}$  [c.f.6-2-B]

The distribution function due to a Fermi surface shift is

$$\delta n_{k\sigma} = n_{k\sigma} - n_{k\sigma}^{(0)} \approx n_{k+q,\sigma}^{(0)} - n_{k\sigma}^{(0)} \approx \vec{q} \cdot \nabla_k n_{k\sigma}^{(0)}$$

The current density is then

$$j_q = \frac{\hbar\vec{q}}{m} \frac{N}{V} = \frac{1}{V} \sum_{k\sigma} \frac{\hbar\vec{k}}{m} \delta n_{k\sigma}$$

Since these two viewpoints have to be equivalent (Galilean invariance), the resulting currents should be the same.

$$\begin{aligned} \frac{\hbar\vec{k}}{m} &= \frac{\hbar\vec{k}}{m^*} + \frac{1}{V} \sum_{k'\sigma'} \delta(\varepsilon_{k'\sigma'} - \varepsilon_F) \frac{\hbar\vec{k}'}{m^*} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \\ \Rightarrow \frac{1}{m} &= \frac{1}{m^*} + g(\varepsilon_F) \int f^s(\hat{k}, \hat{k}') \frac{\hat{k} \cdot \hat{k}'}{m^*} \frac{d\Omega_{\hat{k}'}}{4\pi} \\ &= \frac{1}{m^*} + \frac{1}{m^*} \int g(\varepsilon_F) f^s(\hat{k}, \hat{k}') \cos \theta_{k'} \frac{d\Omega_{\hat{k}'}}{4\pi} \\ &= \frac{1}{m^*} + \frac{1}{m^*} \int \sum_{l=0} F_l^s P_l(\cos \theta_{k'}) P_l(\cos \theta_{k'}) \frac{d\Omega_{\hat{k}'}}{4\pi} \\ &= \frac{1}{m^*} + \frac{1}{m^*} \frac{1}{(2 \times 1 + 1)} F_1^s \\ \Rightarrow \frac{m^*}{m} &= 1 + \frac{1}{3} F_1^s \end{aligned}$$

In general,  $F_1^s > 0$ , the quasiparticle in a Fermi liquid are effectively heavier than bare electrons.

## E. STABILITY OF THE FERMI LIQUID

- (1) Inspection of the renormalization of the quantities

$$\begin{aligned}\frac{\gamma}{\gamma_0} &= \frac{m^*}{m} \\ \frac{\kappa}{\kappa_0} &= \frac{m^*}{m} \frac{1}{1 + F_0^s} \\ \frac{\chi}{\chi_0} &= \frac{m^*}{m} \frac{1}{1 + F_0^a} \\ \frac{m^*}{m} &= 1 + \frac{1}{3} F_1^s\end{aligned}$$

The compressibility and susceptibility diverge for  $F_0^s \rightarrow -1$  and  $F_0^a \rightarrow -1$ , respectively, indicating an instability of the system.

### EXAMPLES:

A diverging spin susceptibility for example leads to a ferromagnetic state with a split Fermi surface, one for each spin direction.

A diverging compressibility leads to a spontaneous contraction of the system.

- (2) More generally, the deformation of the quasiparticle distribution function may vary over the Fermi surface.

Consider a force field  $F$  with conjugate "polarization"  $P$  which yields a modification of the quasiparticle dispersion,

$$\delta\varepsilon_{k\sigma} = -\alpha\lambda_{k\sigma}F \text{ and } \delta\tilde{\varepsilon}_{k\sigma} = -\tilde{\alpha}\lambda_{k\sigma}F$$

Assume that  $\lambda_{k\sigma} = Y_{l,m}(\theta_{\hat{k}}, \phi_{\hat{k}})$  without spin dependence.

$$\begin{aligned}\delta\tilde{\varepsilon}_{k\sigma} &= \delta\varepsilon_{k\sigma} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \delta n_{k'\sigma'} \\ &= \delta\varepsilon_{k\sigma} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \frac{\partial n_{k'\sigma'}}{\partial \tilde{\varepsilon}_{k'\sigma'}} \delta\tilde{\varepsilon}_{k'\sigma'} \\ &= \delta\varepsilon_{k\sigma} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\vec{k}, \vec{k}') \frac{\partial n_{\sigma'}}{\partial \tilde{\varepsilon}_{k'\sigma'}} \delta\tilde{\varepsilon}_{k'\sigma'}\end{aligned}$$

where  $n_{\sigma'}$  is the self-consistent value of the feedback of the quasiparticle coupling.

$$\begin{aligned}
f^{s,a}(\hat{k}, \hat{k}') &= \sum_{l=0} f_l^{s,a} P_l(\hat{k} \cdot \hat{k}') \\
&= 4\pi \sum_{l=0} \frac{f_l^{s,a}}{2l+1} \sum_{m=-l}^l Y_{lm}(\theta_{\hat{k}}, \phi_{\hat{k}}) Y_{lm}^*(\theta_{\hat{k}'}, \phi_{\hat{k}'}) \\
&\Rightarrow \tilde{\alpha} \lambda_{k\sigma} F \\
&= \alpha \lambda_{k\sigma} F - g(\varepsilon_F) \frac{f_l^s}{2l+1} Y_{lm}(\theta_{\hat{k}}, \phi_{\hat{k}}) \tilde{\alpha} \int Y_{lm}^*(\theta_{\hat{k}'}, \phi_{\hat{k}'}) \lambda_{k'\sigma} F d\Omega_{\hat{k}'} \\
&\Rightarrow \tilde{\alpha} = \alpha - \tilde{\alpha} \frac{F_l^s}{2l+1} \\
&\Rightarrow \tilde{\alpha} = \frac{\alpha}{1 + \frac{F_l^s}{2l+1}}
\end{aligned}$$

The polarization is

$$\begin{aligned}
P &= -\frac{1}{V} \sum_{k\sigma} \alpha \lambda_{k\sigma} \delta n_{k\sigma} = -\frac{1}{V} \sum_{k\sigma} \alpha \lambda_{k\sigma} \frac{\partial n_{\sigma'}}{\partial \varepsilon_{k\sigma}} \delta \tilde{\varepsilon}_{k\sigma} = \alpha \tilde{\alpha} g(\varepsilon_F) F \\
\Rightarrow \chi &= \frac{P}{F} = \frac{\alpha^2 g(\varepsilon_F)}{1 + \frac{F_l^s}{2l+1}}
\end{aligned}$$

Stability of the Fermi liquid against any of these deformations requires

$$1 + \frac{F_l^{s,a}}{2l+1} > 0$$

If for any deformation channel  $l$  this conditions is violated one talks about a "Pomeranchuk instability".

# 8-5 First-Principles Calculations

Tuesday, December 20, 2011 8:30 PM

## A. DENSITY FUNCTIONAL THEORY

P. Hohenberg and W. Kohn, *Inhomogeneous Electron Gas*, Phys. Rev. **136**, B864 (1964).

- (1) Many-body problem

$$\mathcal{H} = \sum_i \left( \frac{p_i^2}{2m} + V_{\text{ion}}(\vec{r}_i) \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} = T + V_{\text{ion}} + V_{ee}$$

1. The usual approach to Schrodinger's equation can be summarized as

\* Given  $V_{\text{ion}}$   $\xrightarrow{\mathcal{H}\psi=E\psi} \psi(\vec{r}_1, \vec{r}_2, \dots) = \psi \xrightarrow{\langle \psi | \hat{O} | \psi \rangle}$  observables

One among the observables is the particle density

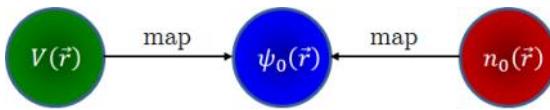
$$n(\vec{r}) = N \int \dots \int \psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) d^3 r_2 \dots d^3 r_N$$

2. The density functional approach can be summarized as

\* Given  $n(\vec{r}) \Rightarrow \psi(\vec{r}_1, \vec{r}_2, \dots) = \psi[n] \xrightarrow{\langle \psi[n] | \hat{O} | \psi[n] \rangle}$  observables  
OS:

The DFT states that for ground states can be inverted: given a groundstate density  $n(\vec{r})$  it is possible, in principle, to calculate the corresponding ground-state wavefunction  $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ . This means that  $\psi$  is a functional of  $n$ . Consequently, all ground-state observables are functionals of  $n$ , too. If  $\psi$  can be calculated from  $n$  and vice versa, both functions are equivalent and contain exactly the same information. At first sight this seems impossible: how can a function of one (vectorial) variable  $\vec{r}$  be equivalent to a function of  $N$  (vectorial) variables  $\vec{r}_1, \dots, \vec{r}_N$ ? How can one arbitrary variable contain the same information as  $N$  arbitrary variables?





(2) Hohenberg-Kohn theorem

The potential  $V_{\text{ion}}(\vec{r})$  is unique functional of the ground state density  $n(\vec{r})$

$\Rightarrow$  One-to-one mapping  $V_{\text{ion}}(\vec{r}) \leftrightarrow n(\vec{r})$ .

**PROOF:**

Suppose  $v$  and  $v'$  give the same ground state density  $n = n'$

$$E_G = \langle \psi_G | \mathcal{H} | \psi_G \rangle$$

$$E'_G = \langle \psi'_G | \mathcal{H} | \psi'_G \rangle$$

If  $E'_G < \langle \psi_G | \mathcal{H}' | \psi_G \rangle$

$$\langle \psi_G | \mathcal{H}' | \psi_G \rangle = \langle \psi_G | \mathcal{H} - v + v' | \psi_G \rangle = E_G + \langle \psi_G | v' - v | \psi_G \rangle$$

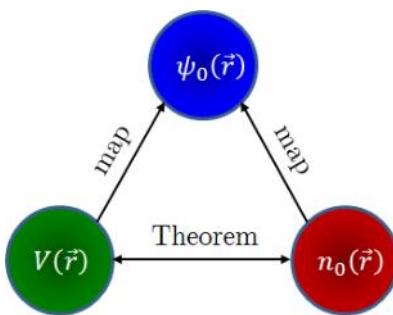
$$\Rightarrow E'_G < E_G + \int n(\vec{r})[v' - v] d^3r$$

If  $E_G < \langle \psi'_G | \mathcal{H} | \psi'_G \rangle$

$$\langle \psi'_G | \mathcal{H} | \psi'_G \rangle = \langle \psi_G | \mathcal{H}' - v' + v | \psi_G \rangle = E'_G + \langle \psi_G | v - v' | \psi_G \rangle$$

$$\Rightarrow E_G < E'_G + \int n(\vec{r})[v - v'] d^3r$$

Add two equations above, we would obtain  $E'_G + E_G < E_G + E'_G$ , a contradiction. There cannot be two different  $v$  that give the same  $n$  for their ground state.



(3) The universal functional

1. The ground state energy  $E = E[n]$

$$E[n] = \underbrace{\mathcal{T}[n] + V[n]}_{F[n]} + V_{\text{ion}}[n] = F[n] + \int n(\vec{r})V_{\text{ion}}(\vec{r}) d^3r$$

$F[n]$  does not depend on the external potential and is the same for all electronic system.

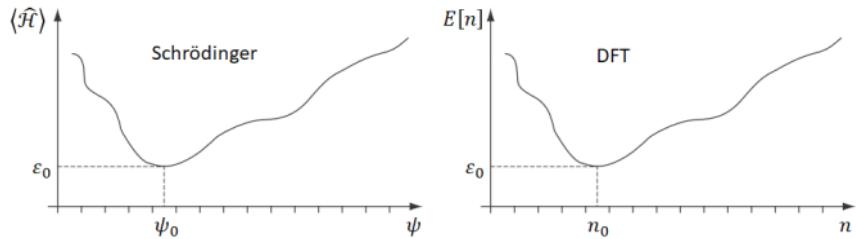
OS:

The explicit form of the functional  $F[n]$  is the major challenge of DFT, i.e., the biggest obstacle is the lack of an accurate expressions for the kinetic energy functional.

2. The true ground state density  $n$  minimizes the energy function  $E[n]$  with the constraint

$$\int n(\vec{r}) d^3r = N$$

$\Rightarrow$  If  $n'$  is not the ground state density, then  $E[n'] > E[n]$



PROOF:

$$E[n'] = \langle \psi'_G | \mathcal{H} | \psi'_G \rangle \geq \langle \psi_G | \mathcal{H} | \psi_G \rangle = E[n]$$

Lagrange multiplier

$$\delta \left( E[n] - \mu \left( N - \int d^3r n(\vec{r}) \right) \right) = 0$$

$$\Rightarrow \frac{\delta F[n]}{\delta n(\vec{r})} + V_{\text{ion}}(\vec{r}) - \mu = 0$$

■

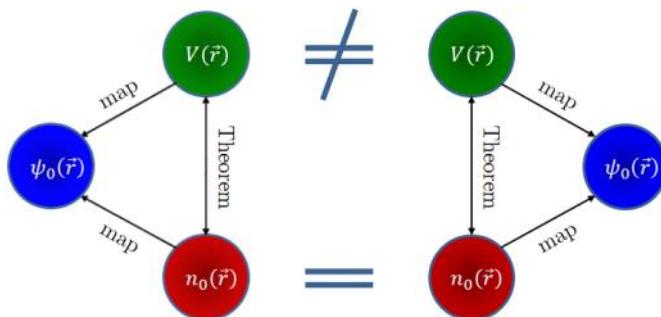
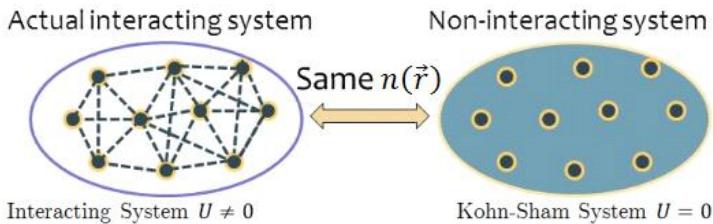
## B. KOHN-SHAM APPROACH

W. Kohn and L.J. Sham, *Self Consistent Equations Including Exchange and Correlation Effects*, Phys. Rev. **140**, A1133 (1965).

- (1) Kohn-Sham electrons

According to the Hohenberg-Kohn theorem, the one-to-one mapping is independent of the electron-electron interaction  $U$ , i.e.,

$$V_{\text{ion}}(\vec{r}) \xleftarrow{U} n(\vec{r}) \xleftarrow{U=0} V_0(\vec{r})$$



## (2) Kohn-Sham approach

### 1. Non-interacting system

Two ways to calculate the density

#### (a) Schrodinger equation

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{ion}}(\vec{r}) \right) \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

#### (b) Euler-Lagrange equation

$$\frac{\delta F_0[n]}{\delta n(\vec{r})} + V_{\text{ion}}(\vec{r}) - \mu = 0$$

where  $F_0[n] = T_0[n]$

### 2. Real system

$$F[n] = T[n] + U[n]$$

$$\begin{aligned} &= (T[n] - T_0[n]) + T_0[n] + U[n] \\ &\quad + \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' - \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' \end{aligned}$$

$$= T_0[n] + \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + E_{\text{xc}}[n]$$

where the exchange-correlation energy

$$E_{\text{xc}}[n] = (T[n] - T_0[n]) + \left( U[n] - \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' \right)$$

Euler-Lagrange equation

$$\begin{aligned} \frac{\delta F[n]}{\delta n(\vec{r})} + V_{\text{ion}}(\vec{r}) - \mu &= 0 \\ \Rightarrow \frac{\delta T_0[n]}{\delta n(\vec{r})} + \frac{e^2}{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})} + V_{\text{ion}}(\vec{r}) - \mu &= 0 \\ \Rightarrow \frac{\delta F_0[n]}{\delta n(\vec{r})} + V_{\text{KS}}(\vec{r}) - \mu &= 0 \end{aligned}$$

where

$$V_{\text{KS}}[n](\vec{r}) = V_{\text{ion}}(\vec{r}) + \frac{e^2}{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})}$$

3. Kohn-Sham equation (to be solved self-consistently)

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{KS}}[n](\vec{r}) \right) \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

$$V_{\text{KS}}[n](\vec{r}) = V_{\text{ion}}(\vec{r}) + \frac{e^2}{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})}$$

Approximate the system locally as homogeneous electron gas  
(Local Density Approximation: LDA)

Ansatz for  $E_{\text{xc}}[n]$

$$E_{\text{xc}}^{\text{LDA}}[n] \approx \int n(\vec{r}) \varepsilon_{\text{xc}}[n] d^3r \Rightarrow \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})} \approx \varepsilon_{\text{xc}}[n]$$

4. Total electronic energy

$$E[n] = \underbrace{\sum_i \varepsilon_i}_{\substack{\text{single} \\ \text{particle} \\ \text{energy}}} - \underbrace{\frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'}_{\text{double counting terms}} - E_{\text{xc}}[n]$$

## C. BASIC EQUATIONS

- (1) Hartree equation

$$\left[ -\frac{\hbar^2}{2m} \nabla_1^2 + V_{\text{ion}}(\vec{r}_1) \right] \psi_k(\vec{r}_1) + \left[ \int \sum_{j \neq k} \psi_j^*(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{r}_2) d^3 r_2 \right] \psi_k(\vec{r}_1) = \varepsilon_k \psi_k(\vec{r}_1)$$

(2) Hartree-Fock equation

$$\left[ -\frac{\hbar^2}{2m} \nabla_1^2 + V_{\text{ion}}(\vec{r}_1) \right] \psi_k(\vec{r}_1) + \int \frac{e^2 n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \psi_k(\vec{r}_1) d^3 r_2 - \int \sum_j \psi_j^*(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{r}_1) \psi_k(\vec{r}_2) d^3 r_2 = \varepsilon_k \psi_k(\vec{r}_1)$$

(3) Kohn-Sham equation

$$\left[ -\frac{\hbar^2}{2m} \nabla_1^2 + V_{\text{ion}}(\vec{r}_1) \right] \psi_k(\vec{r}_1) + \left[ \frac{1}{2} \int \frac{e^2 n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2 + \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r}_1)} \right] \psi_k(\vec{r}_1) = \varepsilon_k \psi_k(\vec{r}_1)$$

# Appendix – Math Background

Tuesday, December 20, 2011 8:22 PM

## A. LAGRANGE MULTIPLIERS

- (2) Simple example

Maxmize the function  $f(x, y) = x + y$  subject to the constraint  $x^2 + y^2 = 1$

- (3) Inelegant approach

1. Solve the constraint equation for  $y$  as a function of  $x$

$$y = \sqrt{1 - x^2}$$

2. Substitute into  $f$ , yielding

$$f(x, y) \equiv \tilde{f}(x) = x + \sqrt{1 - x^2}$$

3. Find the extrema of  $\tilde{f}$  by differentiation

$$\frac{d\tilde{f}(x)}{dx} = 1 - \frac{x}{\sqrt{1 - x^2}} = 0$$

$$x = \frac{1}{\sqrt{2}}, \quad y = \frac{1}{\sqrt{2}}$$

$$\Rightarrow f_{\max} = \sqrt{2}$$

- (4) Elegant approach

1. Write the constraint as  $g(x, y) = 0$

$$g = x^2 + y^2 - 1$$

2. Define  $h = f - \mu g$ , where  $\mu$  is a constant, independent of  $x$  and  $y$

3. Minimize  $h$  freely with no restriction between  $x$  and  $y$

$$\frac{\partial h}{\partial x} = 1 - 2\mu x = 0 \Rightarrow x = \frac{1}{2\mu}$$

$$\frac{\partial h}{\partial y} = 1 - 2\mu y = 0 \Rightarrow y = \frac{1}{2\mu}$$

4. Enforce the condition  $g = 0$

$$\mu = \pm \frac{1}{\sqrt{2}} \text{ (choose the positive sign for a maximum)}$$

$$f_{\max} = x + y = \frac{1}{\mu} = \sqrt{2}$$

This method avoids differentiating square root, etc. This is especially important if we cannot solve the constraint equation analytically.

# Appendix – Slater-Condon Rule

Tuesday, December 20, 2011 8:22 PM

## A. SLATER-CONDON RULE

- (1) The Slater determinant of  $N$  electrons wavefunction representation:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \psi_3(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \psi_3(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \psi_1(\vec{r}_3) & \psi_2(\vec{r}_3) & \psi_3(\vec{r}_3) & \cdots & \psi_N(\vec{r}_3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \psi_3(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

The exchange of two particles is equivalent to the exchange of two columns which produces a change of sign.

state representation:

$$|\Psi\rangle = |\psi_1 \cdots \psi_N\rangle$$

A wavefunction is differed from this by a single orbital

$$|\Psi_p\rangle = |\psi_1 \cdots \psi_p \cdots \psi_N\rangle$$

A wavefunction is differed by two orbitals

$$|\Psi_{pq}\rangle = |\psi_1 \cdots \psi_p \psi_q \cdots \psi_N\rangle$$

A wavefunction is differed by three orbitals

$$|\Psi_{pqr}\rangle = |\psi_1 \cdots \psi_p \psi_q \psi_r \cdots \psi_N\rangle$$

- (2) Slater-Condon rule

- Overlap integral

$$\langle \Psi | \Psi \rangle = 1$$

$$\langle \Psi | \Psi_p \rangle = 0$$

- One-body operator

$$\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi \rangle = \sum_l \langle \psi_l(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_l(\vec{r}_1) \rangle$$

$$\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi_p \rangle = \langle \psi_m(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_p(\vec{r}_1) \rangle$$

$$\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi_{pq} \rangle = 0$$

One body operators have non zero matrix elements only between two determinantal wavefunctions which are either the same or differ in a single one particle wavefunction.

### 3. Two-body operator

$$\begin{aligned} \left\langle \Psi \left| \sum_{i < j}^N V_{ee} \right| \Psi \right\rangle &= \sum_{k < l}^N (\langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) \rangle \\ &\quad - \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_l(\vec{r}_1) \psi_k(\vec{r}_2) \rangle) \\ \left\langle \Psi \left| \sum_{i < j}^N V_{ee} \right| \Psi_p \right\rangle &= \sum_l (\langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_l(\vec{r}_2) \rangle \\ &\quad - \langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_l(\vec{r}_1) \psi_p(\vec{r}_2) \rangle) \\ \left\langle \Psi \left| \sum_{i < j}^N V_{ee} \right| \Psi_{pq} \right\rangle &= \langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_q(\vec{r}_2) \rangle \\ &\quad - \langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | V_{ee} | \psi_q(\vec{r}_1) \psi_p(\vec{r}_2) \rangle \\ \left\langle \Psi \left| \sum_{i < j}^N V_{ee} \right| \Psi_{pqr} \right\rangle &= 0 \end{aligned}$$

Two body operators have non zero matrix elements only between two determinantal wavefunction which are either the same or differ at most in two one particle functions.

## B. PROOF

### (1) Overlap integral

Determinant expansion by minors along the first row

$$\begin{aligned}
& \left| \begin{array}{cccc} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{array} \right| \\
&= \psi_1(\vec{r}_1) \left| \begin{array}{ccc} \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \vdots & \ddots & \vdots \\ \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{array} \right| - \psi_2(\vec{r}_1) \left| \begin{array}{ccc} \psi_1(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{array} \right| \\
&\quad + \cdots + (-1)^{N+1} \psi_N(\vec{r}_1) \left| \begin{array}{ccc} \psi_1(\vec{r}_2) & \cdots & \psi_{N-1}(\vec{r}_2) \\ \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \cdots & \psi_{N-1}(\vec{r}_N) \end{array} \right| \\
&= \sqrt{(N-1)!} \left( \psi_1(\vec{r}_1) |\psi_2 \cdots \psi_N\rangle - \psi_2(\vec{r}_1) |\psi_1 \psi_3 \cdots \psi_N\rangle + \cdots \right. \\
&\quad \left. + (-1)^{N+1} \psi_N(\vec{r}_1) |\psi_1 \cdots \psi_{N-1}\rangle \right) \\
&= \sqrt{(N-1)!} \sum_{i=1}^N (-1)^{i+1} \psi_i(\vec{r}_1) |\psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N\rangle \\
\Rightarrow |\Psi\rangle &= \frac{1}{\sqrt{N}} \sum_{i=1}^N (-1)^{i+1} \psi_i(\vec{r}_1) |\psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N\rangle \\
\langle \Psi | \Psi \rangle &= \langle \psi_1 \cdots \psi_N | \psi_1 \cdots \psi_N \rangle \\
&= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \langle \psi_i(\vec{r}_1) | \psi_j(\vec{r}_1) \rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N | \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \rangle \\
&= \frac{1}{N} \sum_{i=1}^N \langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N | \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N \rangle \\
&= \langle \psi_2 \cdots \psi_N | \psi_2 \cdots \psi_N \rangle = \cdots \cdots \cdots = \langle \psi_N | \psi_N \rangle = 1
\end{aligned}$$

Suppose the determinants differ in one single particle state ( $m$ -th orbitals)

$$|\Psi_p\rangle = |\psi_1 \cdots \psi_p \cdots \psi_N\rangle_{p=m}$$

$$\begin{aligned}
\langle \Psi | \Psi_p \rangle &= \langle \psi_1 \cdots \psi_m \cdots \psi_N | \psi_1 \cdots \psi_p \cdots \psi_N \rangle \\
&= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \langle \psi_i(\vec{r}_1) | \psi_j(\vec{r}_1) \rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N | \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \rangle
\end{aligned}$$

If  $i \neq m$  and  $j \neq p \Rightarrow \langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N | \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \rangle = 0$

If  $i = m$  and  $j = p \Rightarrow \langle \psi_m(\vec{r}_1) | \psi_p(\vec{r}_1) \rangle = 0$

$$\begin{aligned}
\langle \Psi | \Psi_p \rangle &= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \langle \psi_i(\vec{r}_1) | \psi_j(\vec{r}_1) \rangle \\
&\quad \times \underbrace{\langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N | \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \rangle}_{\delta_{im}\delta_{jp}} \\
&= 0
\end{aligned}$$

OS:

Expanding determinant  $|\Psi_p\rangle$  along the  $m$ -th column

$$\begin{aligned}
|\Psi_p\rangle &= \frac{1}{\sqrt{N}} \sum_{i=1}^N (-1)^{i+1} \psi_p(\vec{r}_i) |\psi_1 \cdots \psi_{m-1} \psi_{m+1} \cdots \psi_N\rangle \\
\langle \Psi | \Psi_p \rangle &= \langle \psi_1 \cdots \psi_m \cdots \psi_N | \psi_1 \cdots \psi_p \cdots \psi_N \rangle \\
&= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \langle \psi_m(\vec{r}_i) | \psi_p(\vec{r}_j) \rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{m-1} \psi_{m+1} \cdots \psi_N | \psi_1 \cdots \psi_{m-1} \psi_{m+1} \cdots \psi_N \rangle \\
&= 0
\end{aligned}$$

(2) One-body operator

$$|\Psi\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^N (-1)^{i+1} \psi_i(\vec{r}_k) |\psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N\rangle$$

$$\begin{aligned}
\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi \rangle &= \sum_l \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \left\langle \psi_i(\vec{r}_l) \middle| \hat{h}(\vec{r}_l) \middle| \psi_j(\vec{r}_l) \right\rangle \\
&\quad \times \left\langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N \middle| \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \right\rangle \\
&= \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \underbrace{\left\langle \psi_i(\vec{r}_1) \middle| \hat{h}(\vec{r}_1) \middle| \psi_j(\vec{r}_1) \right\rangle}_{\delta_{ij}} \\
&\quad \times \underbrace{\left\langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N \middle| \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \right\rangle}_{\delta_{ij}} \\
&= \sum_{i=1}^N \langle \psi_i(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_i(\vec{r}_1) \rangle \\
&= \sum_l \langle \psi_l(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_l(\vec{r}_1) \rangle
\end{aligned}$$

Suppose the determinants differ in one wavefunction ( $m$ -th orbitals)

$$\begin{aligned}
|\Psi_p\rangle &= |\psi_1 \cdots \psi_p \cdots \psi_N\rangle_{p=m} \\
\langle \Psi | \sum_l \hat{h}(\vec{r}_l) | \Psi_p \rangle &= \sum_l \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \left\langle \psi_i(\vec{r}_l) \middle| \hat{h}(\vec{r}_l) \middle| \psi_j(\vec{r}_l) \right\rangle \\
&\quad \times \left\langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N \middle| \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \right\rangle \\
&= \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+1} (-1)^{j+1} \underbrace{\left\langle \psi_m(\vec{r}_1) \middle| \hat{h}(\vec{r}_1) \middle| \psi_p(\vec{r}_1) \right\rangle}_{\delta_{im}\delta_{jp}} \\
&\quad \times \underbrace{\left\langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \cdots \psi_N \middle| \psi_1 \cdots \psi_{j-1} \psi_{j+1} \cdots \psi_N \right\rangle}_{\delta_{im}\delta_{jp}} \\
&= \langle \psi_m(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_p(\vec{r}_1) \rangle
\end{aligned}$$

Suppose the determinants differ in two wavefunction ( $m$ -th and  $n$ -th orbitals)

$$\begin{aligned}
|\Psi_{pq}\rangle &= |\psi_1 \cdots \psi_p \psi_q \cdots \psi_N\rangle_{p=m, q=n} \\
&= \frac{1}{\sqrt{N(N-1)}} \sum_{i \neq j}^N (-1)^{i+1} (-1)^{j+1} \psi_i(\vec{r}_k) \psi_j(\vec{r}_k) \\
&\quad \times |\psi_1 \cdots \psi_{i-1} \psi_{i+1} \psi_{j-1} \psi_{j+1} \cdots \psi_N\rangle \\
\langle \Psi | \sum_k \hat{h}(\vec{r}_k) | \Psi_{pq} \rangle &= \sum_k^N \frac{1}{N(N-1)} \sum_{i \neq j}^N (-1)^{i+1} (-1)^{j+1} \sum_{r \neq s}^N (-1)^{r+1} (-1)^{s+1} \\
&\quad \times \langle \psi_i(\vec{r}_k) \psi_j(\vec{r}_k) | \hat{h}(\vec{r}_k) | \psi_r(\vec{r}_k) \psi_s(\vec{r}_k) \rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \psi_{j-1} \psi_{j+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle \\
&= \frac{1}{N-1} \sum_{i \neq j}^N (-1)^{i+1} (-1)^{j+1} \sum_{r \neq s}^N (-1)^{r+1} (-1)^{s+1} \\
&\quad \times \langle \psi_i(\vec{r}_1) \psi_j(\vec{r}_1) | \hat{h}(\vec{r}_1) | \psi_r(\vec{r}_1) \psi_s(\vec{r}_1) \rangle \\
&\quad \times \underbrace{\langle \psi_1 \cdots \psi_{i-1} \psi_{i+1} \psi_{j-1} \psi_{j+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle}_{\delta_{im}\delta_{rp}\delta_{ir}\delta_{js} - \delta_{im}\delta_{sp}\delta_{is}\delta_{jr} + \delta_{jm}\delta_{sp}\delta_{ir}\delta_{js} - \delta_{jm}\delta_{rp}\delta_{is}\delta_{jr}} \\
&= 0
\end{aligned}$$

(3) Two-body operator

$$\begin{aligned}
|\Psi\rangle &= \frac{1}{\sqrt{N(N-1)}} \sum_{k \neq l}^N (-1)^{k+1} (-1)^{l+1} \psi_k(\vec{r}_i) \psi_l(\vec{r}_j) \\
&\quad \times |\psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N\rangle
\end{aligned}$$

$$\begin{aligned}
& \langle \Psi | \sum_{i < j}^N V_{ee} |\Psi \rangle \\
&= \sum_{i < j}^N \frac{1}{N(N-1)} \sum_{k \neq l}^N (-1)^{k+1} (-1)^{l+1} \sum_{r \neq s}^N (-1)^{r+1} (-1)^{s+1} \\
&\quad \times \langle \psi_k(\vec{r}_i) \psi_l(\vec{r}_j) | V_{ee} | \psi_r(\vec{r}_i) \psi_s(\vec{r}_j) \rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle \\
&= \frac{1}{2} \sum_{k \neq l}^N (-1)^{k+1} (-1)^{l+1} \sum_{r \neq s}^N (-1)^{r+1} (-1)^{s+1} \\
&\quad \times \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_r(\vec{r}_1) \psi_s(\vec{r}_2) \rangle \\
&\quad \times \underbrace{\langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle}_{\delta_{kr}\delta_{ls}-\delta_{ks}\delta_{lr}} \\
&= \frac{1}{2} \sum_{k \neq l}^N \left( \langle \psi_k(1) \psi_l(2) | V_{ee} | \psi_k(1) \psi_l(2) \rangle - \langle \psi_k(1) \psi_l(2) | V_{ee} | \psi_l(1) \psi_k(2) \rangle \right) \\
&\quad \times \langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N \rangle \\
&= \sum_{k < l}^N \left( \langle \psi_k(1) \psi_l(2) | V_{ee} | \psi_k(1) \psi_l(2) \rangle - \langle \psi_k(1) \psi_l(2) | V_{ee} | \psi_l(1) \psi_k(2) \rangle \right)
\end{aligned}$$

Suppose the determinants differ in one wavefunction ( $m$ -th orbitals)

$$\begin{aligned}
& \langle \Psi | \sum_{i < j}^N V_{ee} |\Psi_p \rangle \\
&= \sum_{i < j}^N \frac{1}{N(N-1)} \sum_{k=1}^N (-1)^{k+1} \sum_{r=1}^N (-1)^{r+1} \langle \psi_k(\vec{r}_i) \psi_l(\vec{r}_j) | V_{ee} | \psi_r(\vec{r}_i) \psi_s(\vec{r}_j) \rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle \\
&= \frac{1}{2} \sum_{k \neq l}^N (-1)^{k+1} (-1)^{l+1} \sum_{r \neq s}^N (-1)^{r+1} (-1)^{s+1} \\
&\quad \times \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_r(\vec{r}_1) \psi_s(\vec{r}_2) \rangle \\
&\quad \times \underbrace{\langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle}_{\delta_{km}\delta_{rp}\delta_{kr}\delta_{ls}-\delta_{km}\delta_{sp}\delta_{ks}\delta_{lr}+\delta_{lm}\delta_{sp}\delta_{kr}\delta_{ls}-\delta_{lm}\delta_{rp}\delta_{ks}\delta_{lr}}
\end{aligned}$$

where

$$\begin{aligned}
& \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_r(\vec{r}_1) \psi_s(\vec{r}_2) \rangle \\
&= \left( \left\langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_l(\vec{r}_2) \right\rangle - \left\langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_l(\vec{r}_1) \psi_p(\vec{r}_2) \right\rangle \right. \\
&\quad + \left\langle \psi_k(\vec{r}_1) \psi_m(\vec{r}_2) | V_{ee} | \psi_k(\vec{r}_1) \psi_p(\vec{r}_2) \right\rangle \\
&\quad \left. - \left\langle \psi_k(\vec{r}_1) \psi_m(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_k(\vec{r}_2) \right\rangle \right) \\
\left\langle \Psi \middle| \sum_{i < j}^N V_{ee} \right| \Psi_p \rangle &= \sum_l \left( \left\langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_l(\vec{r}_2) \right\rangle \right. \\
&\quad \left. - \left\langle \psi_m(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_l(\vec{r}_1) \psi_p(\vec{r}_2) \right\rangle \right)
\end{aligned}$$

Suppose the determinants differ in two wavefunction ( $m$ -th and  $n$ -th orbitals)

$$\begin{aligned}
& \left\langle \Psi \middle| \sum_{i < j}^N V_{ee} \right| \Psi_{pq} \rangle \\
&= \sum_{i < j}^N \frac{1}{N(N-1)} \sum_{k=1}^N (-1)^{k+1} \sum_{r=1}^N (-1)^{r+1} \left\langle \psi_k(\vec{r}_i) \psi_l(\vec{r}_j) \middle| V_{ee} \middle| \psi_r(\vec{r}_i) \psi_s(\vec{r}_j) \right\rangle \\
&\quad \times \langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle \\
&= \frac{1}{2} \sum_{k \neq l}^N (-1)^{k+1} (-1)^{l+1} \sum_{r \neq s}^N (-1)^{r+1} (-1)^{s+1} \\
&\quad \times \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_r(\vec{r}_1) \psi_s(\vec{r}_2) \rangle \\
&\quad \times \underbrace{\langle \psi_1 \cdots \psi_{k-1} \psi_{k+1} \psi_{l-1} \psi_{l+1} \cdots \psi_N | \psi_1 \cdots \psi_{r-1} \psi_{r+1} \psi_{s-1} \psi_{s+1} \cdots \psi_N \rangle}_{\delta_{km}\delta_{ln}\delta_{rp}\delta_{sq} - \delta_{km}\delta_{ln}\delta_{rq}\delta_{sp} + \delta_{kn}\delta_{lm}\delta_{rq}\delta_{sp} - \delta_{kn}\delta_{lm}\delta_{rp}\delta_{sq}} \\
&\quad \text{where}
\end{aligned}$$

$$\begin{aligned}
& \langle \psi_k(\vec{r}_1) \psi_l(\vec{r}_2) | V_{ee} | \psi_r(\vec{r}_1) \psi_s(\vec{r}_2) \rangle \\
&= \left( \left\langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_q(\vec{r}_2) \right\rangle - \left\langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | V_{ee} | \psi_q(\vec{r}_1) \psi_p(\vec{r}_2) \right\rangle \right. \\
&\quad + \left\langle \psi_n(\vec{r}_1) \psi_m(\vec{r}_2) | V_{ee} | \psi_q(\vec{r}_1) \psi_p(\vec{r}_2) \right\rangle \\
&\quad \left. - \left\langle \psi_n(\vec{r}_1) \psi_m(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_q(\vec{r}_2) \right\rangle \right) \\
\left\langle \Psi \middle| \sum_{i < j}^N V_{ee} \right| \Psi_{pq} \rangle &= \left\langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | V_{ee} | \psi_p(\vec{r}_1) \psi_q(\vec{r}_2) \right\rangle \\
&\quad - \left\langle \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) | V_{ee} | \psi_q(\vec{r}_1) \psi_p(\vec{r}_2) \right\rangle
\end{aligned}$$

Suppose the determinants differ in three wavefunction ( $m$ -th,  $n$ -th, and  $o$ -th orbitals)

$$\left\langle \Psi \left| \sum_{i < j}^N V_{ee} \right| \Psi_{pqr} \right\rangle = 0$$

■

# Appendix – Lifetime of Quasiparticles at Finite Temperature

Tuesday, December 20, 2011 8:22 PM

- (1) The lifetime  $\tau_k$

$$\begin{aligned} \frac{1}{\tau_k} &= \frac{2\pi}{\hbar} \frac{1}{V^2} \sum_{k',q} \left| \left\langle \vec{k} \left| \hat{V}_q \right| \vec{k} - \vec{q}, \vec{k}' + \vec{q}, \vec{k}' \right\rangle \right|^2 f_{k'} (1 - f_{k'+q}) (1 - f_{k-q}) \\ &\quad \times \delta \left( (\varepsilon_{k'+q} - \varepsilon_{k'}) - (\varepsilon_k - \varepsilon_{k-q}) \right) \\ &= \frac{2\pi}{\hbar} \int \int |V(q)|^2 f_{k'} (1 - f_{k'+q}) (1 - f_{k-q}) \\ &\quad \times \delta \left( (\varepsilon_{k'+q} - \varepsilon_{k'}) - (\varepsilon_k - \varepsilon_{k-q}) \right) \frac{d^3 q}{(2\pi)^3} \frac{d^3 k'}{(2\pi)^3} \end{aligned}$$

- (2) Introduce the energy transfer

$$\begin{aligned} \varepsilon &= \varepsilon_k - \varepsilon_{k-q} = \varepsilon_{k'+q} - \varepsilon_{k'} \\ \delta \left( (\varepsilon_{k'+q} - \varepsilon_{k'}) - (\varepsilon_k - \varepsilon_{k-q}) \right) &= \int_{-\infty}^{\infty} \delta(\varepsilon_{k'+q} - \varepsilon_{k'} - \varepsilon) \delta(\varepsilon_k - \varepsilon_{k-q} - \varepsilon) d\varepsilon \\ \frac{1}{\tau_k} &= \frac{2\pi}{\hbar} \int \int \int_{-\infty}^{\infty} |V(q)|^2 f(\varepsilon_{k'}) (1 - f(\varepsilon_{k'} + \varepsilon)) (1 - f(\varepsilon_k - \varepsilon)) \\ &\quad \times \delta(\varepsilon_{k'+q} - \varepsilon_{k'} - \varepsilon) \delta(\varepsilon_k - \varepsilon_{k-q} - \varepsilon) \frac{d^3 q}{(2\pi)^3} \frac{d^3 k'}{(2\pi)^3} d\varepsilon \\ \delta(\varepsilon_k - \varepsilon_{k-q} - \varepsilon) &= \delta \left( \frac{\hbar^2 k q \cos \theta}{m} - \frac{\hbar^2 q^2}{2m} - \hbar \omega \right) \\ \delta(\varepsilon_{k'+q} - \varepsilon_{k'} - \varepsilon) &= \delta \left( \frac{\hbar^2 k' q \cos \theta'}{m} + \frac{\hbar^2 q^2}{2m} - \hbar \omega \right) \\ \frac{1}{\tau_k} &= \frac{2\pi}{\hbar} \int \int \int_{-\infty}^{\infty} |V(q)|^2 f(\varepsilon_{k'}) (1 - f(\varepsilon_{k'} + \varepsilon)) (1 - f(\varepsilon_k - \varepsilon)) \\ &\quad \times \delta \left( \frac{\hbar^2 k q \cos \theta}{m} - \frac{\hbar^2 q^2}{2m} - \hbar \omega \right) \delta \left( \frac{\hbar^2 k' q \cos \theta'}{m} + \frac{\hbar^2 q^2}{2m} - \hbar \omega \right) \\ &\quad \times \frac{q^2 dq}{(2\pi)^2} d(\cos \theta) \frac{k'^2 dk'}{(2\pi)^2} d(\cos \theta') d\varepsilon \end{aligned}$$

- (3) The energy transfer is small. We can neglect  $\omega$  in the arguments of the

$\delta$  function, but keep it in the arguments of the Fermi functions because there  $\omega$  is divided by  $T$ .

OS:

With  $\omega = 0$  in the  $\delta$  function, the values of the cosines are

$$\cos \theta = \frac{q}{2k}, \quad -\cos \theta' = \frac{q}{2k'}$$

Since  $q \ll k_F$

$$\cos \theta \approx \frac{q}{2k_F} \ll 1, \quad -\cos \theta' \approx \frac{q}{2k_F} \ll 1,$$

Therefore

$$-1 < \cos \theta, \cos \theta' < 1$$

$$\begin{aligned} \frac{1}{\tau_k} &= \frac{2\pi}{\hbar} \int \int \int_{-\infty}^{\infty} |V(q)|^2 \frac{m}{\hbar^2 k_F q} \frac{m}{\hbar^2 k_F q} \frac{q^2 dq}{(2\pi)^2} \\ &\quad \times f(\varepsilon_{k'}) (1 - f(\varepsilon_{k'} + \varepsilon)) (1 - f(\varepsilon_k - \varepsilon)) \frac{k'^2 dk'}{(2\pi)^2} d\varepsilon \\ &= \frac{1}{8\pi^3 \hbar^2 v_F^2} \int |V(q)|^2 dq \\ &\quad \times \int \int_{-\infty}^{\infty} f(\varepsilon_{k'}) (1 - f(\varepsilon_{k'} + \varepsilon)) (1 - f(\varepsilon_k - \varepsilon)) k'^2 dk' d\varepsilon \end{aligned}$$

As  $k'$  is near  $k_F$

$$\int_0^{\infty} k'^2 dk' \approx \int_0^{\infty} k_F^2 d(k' - k_F) = \frac{k_F^2}{\hbar v_F} \int_{-\infty}^{\infty} d\xi_{k'}$$

where  $\xi_{k'} = v_F \hbar (k' - k_F)$  is the energy of excitation measured from the Fermi energy.

$$\begin{aligned} \frac{1}{\tau_k} &= \frac{k_F^2}{8\pi^3 \hbar^3 v_F^3} \int |V(q)|^2 dq \\ &\quad \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\xi_{k'}) (1 - f(\xi_{k'} + \varepsilon)) (1 - f(\xi_k - \varepsilon)) d\xi_{k'} d\varepsilon \end{aligned}$$

Since

$$\int_{-\infty}^{\infty} f(\xi_{k'}) (1 - f(\xi_{k'} + E)) d\xi_{k'} = \frac{\varepsilon}{1 - e^{-\varepsilon/k_B T}}$$

$$\begin{aligned} \frac{1}{\tau_k} &= \frac{k_F^2}{8\pi^3 \hbar^3 v_F^3} \int |V(q)|^2 dq \int_{-\infty}^{\infty} \frac{\varepsilon}{1 - e^{-\varepsilon/k_B T}} \left( 1 - \frac{1}{e^{(\xi_k - \varepsilon)/k_B T} + 1} \right) d\varepsilon \\ &= \frac{k_F^2}{8\pi^3 \hbar^3 v_F^3} \int |V(q)|^2 dq \int_{-\infty}^{\infty} \frac{\varepsilon}{1 - e^{-\varepsilon/k_B T}} \frac{1}{e^{(\varepsilon - \xi_k)/k_B T} + 1} d\varepsilon \end{aligned}$$

Let  $y = E/k_B T$

$$\frac{1}{\tau_k} = \frac{k_B^2 T^2 k_F^2}{8\pi^3 \hbar^3 v_F^3} \int |V(q)|^2 dq F(\xi_k/T)$$

where

$$\begin{aligned} F(x) &= \int_{-\infty}^{\infty} \frac{y}{(e^{y-x} + 1)(1 - e^{-y})} dy = \frac{x^2 + \pi^2}{2} \frac{1}{1 + e^{-x}} \\ \frac{1}{\tau_k} &= \frac{k_B^2 T^2 k_F^2}{8\pi^3 \hbar^3 v_F^3} \frac{(\xi_k/k_B T)^2 + \pi^2}{2} \frac{1}{1 + e^{-\xi_k/k_B T}} \int |V(q)|^2 dq \\ &= \frac{k_F^2}{8\pi^3 \hbar^3 v_F^3} \frac{\xi_k^2 + \pi^2 k_B^2 T^2}{2} \frac{1}{1 + e^{-\xi_k/k_B T}} \int |V(q)|^2 dq \end{aligned}$$

EXAMPLES:

For a particle right on the Fermi surface ( $\xi_k = 0$ ),

$$\begin{aligned} F(0) &= \int_{-\infty}^{\infty} \frac{y}{(e^y + 1)(1 - e^{-y})} dy = \int_0^{\infty} \frac{y}{\sinh y} dy = \frac{\pi^2}{4} \\ \frac{1}{\tau_k} &= \frac{k_B^2 T^2 k_F^2}{8\pi^3 \hbar^3 v_F^3} \int |V(q)|^2 dq \frac{\pi^2}{4} = \frac{k_B^2 T^2 k_F^2}{32\pi \hbar^3 v_F^3} \int |V(q)|^2 dq \end{aligned}$$

For a screened Coulomb potential

$$\int_0^{\infty} |V(q)|^2 dq = \int_0^{\infty} \left( \frac{e^2}{\epsilon_0 q^2 + q_0^2} \right)^2 dq = \frac{e^4}{\epsilon_0^2} \frac{\pi}{4q_0^3}$$

OS:

$$\begin{aligned} \int_0^{\infty} \frac{dx}{(q^2 + a^2)} &= \left[ \frac{q}{2a^2(q^2 + a^2)} + \frac{1}{2a^3} \tan^{-1} \frac{q}{a} \right]_0^{\infty} \\ &= \frac{1}{2a^3} \frac{\pi}{2} \\ &= \frac{\pi}{4a^3} \end{aligned}$$

$$g(\varepsilon_F) = \frac{mk_F}{\pi^2 \hbar^2} = \frac{k_F^2}{\pi^2 \hbar v_F}$$

$$\text{Let } \kappa = e^4 / \epsilon_0^2 q_0^3$$

$$\frac{1}{\tau} = \frac{k_B^2 T^2 k_F^2}{32\pi \hbar^3 v_F^3} \frac{e^4}{\epsilon_0^2} \frac{\pi}{4q_0^3} = \frac{\pi^2}{128} \frac{\kappa}{v_F^2} \frac{k_B^2 T^2}{\hbar^2 g(\varepsilon_F)} \propto T^2$$