

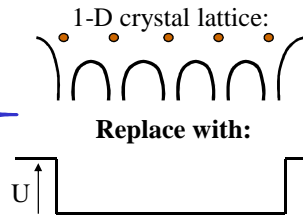
## Drude (classical) model: The simplest!

### Metals! – definition...?

The Drude model describes the electrical and thermal conductivity of metals – its an application of the kinetic theory of gases

*Coulomb potential energy of positive ions is screened by bound electrons and is weaker at large distances from nucleus. Electron-electron interactions also ignored.*

**Electrons would have lowest U (highest K) near nuclei, so they spend less time near nuclei and more time far from nuclei where U is not changing rapidly**



*An electron that experiences a uniform E-field and accelerates indefinitely and imply an increasing current !!*

*Assume that resistance comes from electrons interacting with periodic lattice through occasional collisions with the ions (Drift velocity  $v_d$ , collision/relaxation time  $\tau$ )*



## Heat Capacity of the Classical (Drude) FEG

The result is a constant average velocity:

$$\sum F_x = m \frac{d^2x}{dt^2} = -eE + F_{coll} \quad \xrightarrow{\text{Hint: } F_{coll} = -mv/\tau} \quad v = v_d = \frac{-eE\tau}{m}$$

And the current density of electrons (charge,  $e$ ) can easily be calculated to be:  $J = -nev$

Combined, these equations yield Ohm's Law and the definition of electrical conductivity,  $\sigma$   $J = \left(\frac{ne^2\tau}{m}\right)E = \sigma E$  **Drude model gets this correct!**

But if this classical model is used to determine heat capacity,  $C_{el} \dots$

Each monatomic gas molecule in a sample at temperature  $T$  has energy  $\frac{3}{2}k_B T$ , so total energy per mole is  $\epsilon'_{el} = \frac{3}{2}N_A k_B T = \frac{3}{2}RT \rightarrow C_{el} = d(\epsilon'_{el})/dT = \frac{3}{2}R$

But experiments show that the electronic specific heat is  $<1\%$  of that expected from classical theory and does not explain its temperature dependence.



## A success of the classical description

- It yields a seemingly (near) correct description of the Wiedemann-Franz Law
  - experimentally the ratio of thermal and electrical conductivity for metals is constant at a given temperature.
  - This constant,  $L$ , is the Lorenz number
  - The Drude theory gives  $L = 3k_B^2/2e^2$
  - *Check this! Use  $\sigma$  from previous slide, and the thermal conductivity of a classical gas of electrons – this assumption works well since the electrons dominate in metals.*
  - (Note,  $L$  calculated in this manner is actually too small by a factor of  $\sim 2$ )

$$\frac{K}{\sigma} = LT$$

## So why is the classical description not good enough?



- Ohm's Law
- Wiedemann-Franz Law



- Heat capacity\*
- (Magnetic susceptibility\*)
- Mean free paths of electrons in pure, cold specimens are  $\sim 10^8$  interatomic spacings – undeflected by collisions!
  - Matter waves can propagate freely in a periodic structure (Bloch – later!)
  - Conduction electrons are scattered only infrequently by other conduction electrons  $\rightarrow$  Fermi statistics/Pauli

\* Due to failure of classical Maxwellian distribution function, not of free electron approx

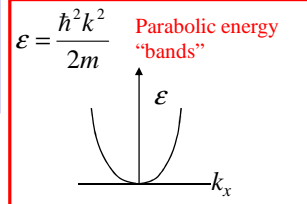
## A better model: The Quantum (Fermi) free electron description

Consider one-electron problem by assuming the interaction between electrons is insignificant, and look for solutions in 1D using the time-independent SE equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + U \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

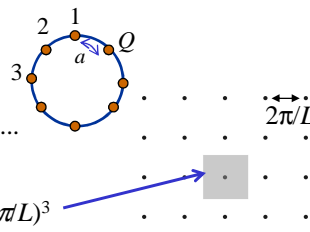
With  $U=0 \rightarrow \nabla^2 \psi = -k^2 \psi$

Solutions:  $\psi = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$   
 Traveling waves (plane waves):  
 propagates like a free particle



By using **periodic boundary conditions\*** for a cubic solid with arbitrary edge length  $L=Qa$ , we define the set of allowed wave vectors

$$k_x = \frac{2\pi n_x}{L} \quad k_y = \frac{2\pi n_y}{L} \quad k_z = \frac{2\pi n_z}{L} \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \pm 3, \dots$$



$\rightarrow$  Volume of 1<sup>st</sup> BZ is  $(2\pi L)^3$

\*  $\psi(x+L, y, z) = \psi(x, y, z)$  etc

## Properties of the QFEG model: Density of states (DOS), $G(\epsilon)$

We often need to know the DOS,  $G(\epsilon) = dN_s/d\epsilon$  in order to calculate the number of charge carriers that can contribute to the conduction process.

- # of allowed states in range  $k \rightarrow k + dk = (\text{vol of } k\text{-space}) / (\text{vol of one } k\text{-state})$

$$G(k)dk = 2 \times \left( \frac{4\pi k^2 dk}{(2\pi/L)^3} \right)$$

← volume of spherical shell in  $k$ -space  
 ← volume of 1st BZ (in  $k$ -space)

two spin electron states (fermions)

- Therefore  $G(\epsilon) = dN_s/d\epsilon = (G(k)dk)/d\epsilon = [V(2m)^{3/2}/2\pi^2\hbar^3] \epsilon^{1/2}$  i.e.  $G(\epsilon_F) \propto \epsilon^{1/2}$

- We can define the **Fermi Energy,  $\epsilon_F$**  as the **energy of the highest filled electron state at  $T = 0\text{K}$**

# of electrons  $= N_e = \int_0^{\epsilon_F} G(\epsilon) d\epsilon \rightarrow \epsilon_F = \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N_e}{V} \right)^{2/3}$

- By combining the equations for  $\epsilon_F$  and  $G(\epsilon)$  above, one can also write

$$G(\epsilon_F) = dN_e/d\epsilon = \frac{3N_e}{2\epsilon_F}$$

## The Fermi-Dirac Distribution function:

a probability function that applies to an ideal gas of fermions (FEG)

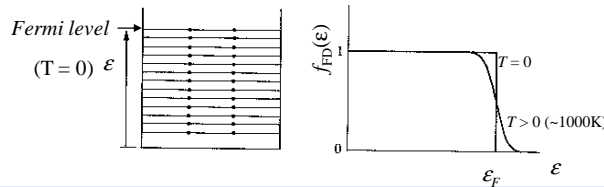
- The occupation of electron states is governed by the Pauli exclusion principle, and that the probability of occupation of a state with energy  $\epsilon$  at temperature  $T$  is:

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

where  $\mu(T)$  = chemical potential

The **chemical potential** of a thermodynamic system is the amount by which the energy of the system would change if an additional particle were introduced, with the entropy and volume held fixed.

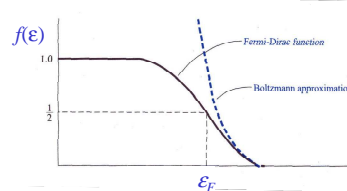
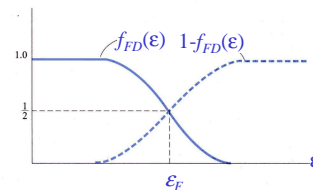
- At absolute zero,  $\mu = \epsilon_F$  because in the limit  $T \rightarrow 0$ ,  $f_{FD}(\epsilon)$  changes discontinuously from 1 (filled) to 0 (empty)
- The Fermi level is the label given to the state which has  $f_{FD}(\epsilon) = 1/2$  (i.e. when  $\epsilon = \mu$ )
- When  $k_B T \ll \epsilon_F$  (which includes room temperature) we ignore the temperature dependence of  $\mu$ , and replace it with  $\epsilon_F$ .



## Electron Distribution

$$f_{FD}(\epsilon) = \frac{1}{\exp[(\epsilon - \epsilon_F)/k_B T] + 1}$$

- Notice **SYMMETRY** i.e. The probability of a state a distance  $d\epsilon$  above  $\epsilon_F$  being occupied is the same as the probability of a state  $d\epsilon$  below  $\epsilon_F$  being empty,
- Also notice the **SIMPLIFICATION** when  $\epsilon - \epsilon_F \gg k_B T$ , the exponential term in the denominator of the Fermi-Dirac probability function is much greater than 1.



$$f_{FD}(\epsilon) \approx \exp\left[\frac{-(\epsilon - \epsilon_F)}{k_B T}\right]$$

Maxwell-Boltzmann approximation

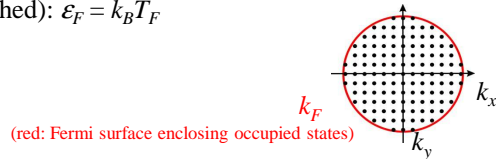
**MB and FD functions are within 5% of each other when  $\epsilon - \epsilon_F = 3k_B T$**



## Fermi temperature, $T_F$ and Fermi wavevector, $k_F$

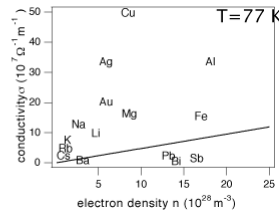
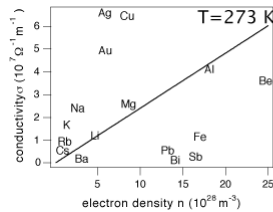
- For temperatures above  $T_F$ , the free electron gas will act as a classical gas rather than being dominated by the Pauli Exclusion Principle (most metals will vaporise before  $T_F$  is reached):  $\epsilon_F = k_B T_F$

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



- The occupied states of the FEG (isotropic) are described by k-values in a sphere of radius  $k_F$  (Fermi Sphere – Fermi surface)

- The average velocity of an electron in an atom at absolute zero - Fermi velocity  $v_F = \left( \frac{2\epsilon_F}{m} \right)^{1/2}$ 
  - atomic ionisation energies
  - reciprocal of atomic spacing
- For a typical metal, with electron density ( $N/V$ )  $\sim 10^{28} \text{m}^{-3}$ ,  $\epsilon_F \sim 2\text{eV}$  and  $k_F \sim 6.7 \text{nm}^{-1}$ ,  $T_F \sim 10^5 \text{K}$ ,  $v_F \sim 10^6 \text{ms}^{-1}$



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

Relaxation time calculated for a fixed mean free path and a T-dependent thermal velocity.

i.e. Relaxation time increases for lower T

The assumption of a fixed mean free path (given by interatomic spacing) is WRONG!! (it can become macroscopic!)