# Band Theory and Electronic Properties of Solids

# Phys 674

Physics & Astronomy
King Saud University

$2^{nd}$ Term: 2025

## Week No. 04

**The Sommerfeld Theory of Metals Part II**

*Prof. Nasser S. Alzayed*

# Ground state properties of the e-Gas

① let us assume $N$ electrons inside Fermi sphere $K < K_F$

② Total Energy $E$ is:

$$E = 2 \sum_{K<K_F} \frac{\hbar^2}{2m} K^2 \qquad \text{--- (2.14)}$$

2 is due to two spin states.

③ let $\frac{\hbar^2}{2m} K^2 \equiv F(\bar{K})$

and $\Delta K = \frac{8\pi^3}{V}$ (size of smallest Volume in K-space)

(4) $\Rightarrow \sum_{k} F(k) = \frac{V}{8\pi^3} \sum F(k)\, \Delta K \quad (2.15)$

Cancel each other

(5) if $V$ is Large $V \to \infty$

$\rightarrow \quad \sum \rightarrow \int$

$\therefore \quad \sum_{k} F(k)\, \Delta K \rightarrow \int F(k)\, d^3k$

$\therefore (2.15) \rightarrow \quad \lim_{V\to\infty} \frac{1}{V} \sum F(k) = \int \frac{d\bar{k}}{8\pi^3} F(k) \quad --(2.16)$

(6) (2.14) $\Rightarrow$

$$\frac{E}{V} = \frac{1}{4\pi^3}\int d\bar{k}\,\frac{\hbar^2 k^2}{2m}$$

$$= \frac{\hbar^2}{8m\pi^3}\int d\bar{k}\,k^2$$

$$= \frac{\hbar^2}{8m\pi^3}\int k^2\left(k^2 \sin\theta\, d\theta\, d\phi\, dk\right)$$

$$= \frac{\hbar^2}{8m\pi^3}\underbrace{\int \sin\theta\, d\theta\, d\phi}_{=4\pi}\int k^4\, dk$$

$$= \frac{\hbar^2}{\cancel{8}m\pi^{3}}\cdot\cancel{4\pi}\cdot\frac{k_F^5}{5}$$

2 2

$$\therefore\ \frac{E}{V} = \frac{1}{\pi^2}\cdot\frac{\hbar^2 k_F^5}{10m} \qquad (**)$$

⑦ To find Energy/e $= \frac{E}{V}$

we devide by $\frac{N}{V} = n$

$$\therefore \frac{\frac{E}{V}}{\frac{N}{V}} = \frac{E}{V} \times \frac{V}{N} = \frac{E}{N} = \frac{1}{\cancel{\pi^2}} \frac{\hbar^2 K_F^5}{10m} \div \frac{\cancel{K_F^3}}{3\cancel{\pi^2}}$$

$$\therefore \frac{E}{N} = \frac{3}{5} \cdot \frac{\hbar^2 K_F^2}{2m}$$

$$\therefore \frac{E}{N} = \frac{3}{5} \cdot \epsilon_F \qquad \text{-----} (2.16)$$

$$= \frac{3}{5} K_B T_F$$

# GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- To calculate *the ground-state energy of N electrons* in a volume *V* we must add up the energies of all the one-electron levels inside the Fermi sphere:

$$E = 2\sum_{k<k_F} \frac{\hbar^2}{2m} k^2 \tag{2.14}$$

- We need to do summing of F(**k**) over all values of **k**
- Because the volume of k-space per allowed **k** value is: $\Delta\boldsymbol{k} = \frac{8\pi^3}{V}$

$$\sum_{k} F(\mathbf{k}) = \frac{V}{8\pi^3}\sum_{k} F(\mathbf{k})\Delta\mathbf{k} \tag{2.15}$$

- for in the limit as $\Delta\boldsymbol{k} \to 0 (V \to \infty)$ the sum $\sum F(\boldsymbol{k})\Delta\boldsymbol{k}$ approaches the integral $\int$ F(**k**)$d\boldsymbol{k}$:

$$\lim_{V\to\infty} \frac{1}{V}\sum_{k} F(\mathbf{k}) = \int \frac{d\mathbf{k}}{8\pi^3} F(\mathbf{k}) \tag{2.16}$$

# GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- From Eq. (2.16) in Eq. (2.14): We find *the energy density of the electron gas*:

$$\frac{E}{V}=\frac{1}{4\pi^3}\int d\mathbf{k}\,\frac{\hbar^2 k^2}{2m}=\frac{1}{4\pi^3}\frac{\hbar^2}{2m}\int d\mathbf{k}k^2=\frac{1}{4\pi^3}\frac{\hbar^2}{2m}\int (k^2 sin\theta d\theta d\phi dk)k^2$$

$$\frac{1}{4\pi^3}\frac{\hbar^2}{2m}\int sin\theta d\theta d\phi\int k^2 dk k^2=\frac{1}{4\pi^3}\frac{\hbar^2}{2m}(4\pi)\frac{k_F^5}{5}$$

$$=\frac{1}{\pi^2}\frac{\hbar^2 k_F^5}{10m}$$

- To find *the energy per electron*, E/N, in the ground state, we must divide this by N/V:

$$\frac{E}{N}=\frac{1}{\pi^2}\frac{\hbar^2 k_F^5}{10m}\div\frac{k_F^3}{3\pi^2}=\frac{3\hbar^2 k_F^2}{10m}=\frac{3}{5}\varepsilon_F$$

$$\rightarrow\frac{E}{N}=\frac{3}{5}k_B T_F \qquad (2.16)^*$$

⑧ To find the Pressure of Electron Gas:

$$\because \quad P = -\frac{\partial E}{\partial V} \quad \text{-----} \quad (1)$$

(2.16) $\Rightarrow$ $\because \quad E = \frac{3}{5} N \epsilon_F \quad \text{——} \quad (2)$

$\because$ No. of states / unit volume ($\equiv$ density)

$$= \frac{V}{8\pi^3}$$

$$\because \quad N = \frac{V}{\underset{(2)}{\cancel{8}}\, \pi^{\cancel{3}\,2}} \cdot \frac{\cancel{4}\,\cancel{\pi}}{3} k_F^3 \quad (3)$$ (total No. of states)

$\because \quad \frac{4}{3} \pi k_F^3 \equiv$ volume of Fermi sphere

$$(3) \rightarrow \quad k_F^3 = \frac{3N\pi^2}{V} \quad \text{-} \quad (4)$$ (2 was Cancelled for spin issue)

(4) in (2):

$$E = \frac{3}{5} N \cdot \frac{\hbar^2 k_F^2}{2m} = \frac{3}{5} \cdot N \frac{\hbar^2}{2m} \left( \frac{3N\pi^2}{V} \right)^{2/3} \quad \cdots (5)$$

$$\therefore P = -\frac{\partial E}{\partial V} = -\frac{3}{5} \cdot N \cdot \frac{\hbar^2}{2m} (3N\pi^2)^{2/3} \frac{\partial}{\partial V} (V)^{-2/3}$$

$$= \cancel{-} \frac{\cancel{3}}{5} \cdot N \cdot \frac{\hbar^2}{\cancel{2}m} (3N\pi^2)^{2/3} \left(\cancel{-} \frac{\cancel{2}}{\cancel{3}}\right) (V)^{-5/3}$$

$$= \cancel{N} \cdot \frac{\hbar^2}{5m} \frac{(3N\pi^2)^{5/3}}{3\cancel{N}\pi^2} \left(\frac{1}{V}\right)^{5/3}$$

$$= \frac{\hbar^2}{5m} \frac{1}{3\pi^2} \left( \frac{3N\pi^2}{V} \right)^{5/3}$$

$$\therefore \boxed{P = \frac{2}{3} \cdot \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}} \quad \cdots (6)$$

## *GROUND-STATE PROPERTIES OF THE ELECTRON GAS*

- One can calculate *the pressure exerted by the electron gas* from the relation: $P=-(\partial E/\partial V)_N$

$$P=-\left(\frac{\partial E}{\partial V}\right)$$

$$\text{using: } E=\frac{3}{5}N\varepsilon_F \;\;\&\;\; \varepsilon_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\Rightarrow E=\frac{3}{5}N\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\Rightarrow P=\frac{2}{3}\frac{E}{V}$$

$$\Rightarrow P=\frac{2}{3}.\frac{1}{\pi^2}\frac{\hbar^2 k_F^5}{10m}$$

9 to Find Compressibility $K$ and Bulk modulus $B$

(Prove)

$$\because B = \frac{5}{3} P = \frac{2}{3} \frac{N}{V} \epsilon_F \quad \text{--- } 7$$

$$\Rightarrow K = \frac{1}{B} = \frac{3}{2} \frac{V}{N} \frac{1}{\epsilon_F} \quad \text{--- } 8$$

# GROUND-STATE PROPERTIES OF THE ELECTRON GAS

- *Compressibility*, K, can be derived as well:

$$B = \frac{1}{K} = -V\left(\frac{\partial P}{\partial V}\right)$$

$$\Rightarrow B = \frac{5}{3}P = \frac{2}{3}\frac{N}{V}\varepsilon_F$$

- Please prove the above relation.
- *B is called Bulk modulus*

BULK MODULI IN $10^{10}$ DYNES/CM$^2$ FOR SOME TYPICAL METALS[a]

| METAL | FREE ELECTRON $B$ | MEASURED $B$ |
|---|---|---|
| Li | 23.9 | 11.5 |
| Na | 9.23 | 6.42 |
| K | 3.19 | 2.81 |
| Rb | 2.28 | 1.92 |
| Cs | 1.54 | 1.43 |
| Cu | 63.8 | 134.3 |
| Ag | 34.5 | 99.9 |
| Al | 228 | 76.0 |

[a] The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

the Figure is our First test of the FEM:

we see that FEM Also fails in B calculation

But its failure is more as the atomic size increases.

Compare Li or Na with AL.

why it fails?

(1) it did not account for ionic core Interact.

(2) in large atoms such as Cu, Ag ...

d-electrons interact strongly with lattice

(3) it ignores Bonding Contribution..

Al has Covalent Bonding $\Longrightarrow$ increase of B

(4) FEM did not include any effect of Bonding at all.

(5) Crystal lattice Contribution:
Lattice is very important when it comes to B-Modulus.
for instance FCC has more stiffness than BCC.
the FEM has no Consideration of all of that.

(6) FEM: did not include e-e Interaction
the model (like Drude) did not include any e-e interactions.

?) FEM: it assumes uniform density of states for electrons.

this is valid only to s-electrons.

for d-states: density is not uniform

**Table 4 Comparison of observed Hall coefficients with free electron theory**

[The experimental values of $R_H$ as obtained by conventional methods are summarized from data at room temperature presented in the Landolt-Bornstein tables. The values obtained by the helicon wave method at 4 K are by J. M. Goodman. The values of the carrier concentration $n$ are from Table 1.4 except for Na, K, Al, In, where Goodman's values are used. To convert the value of $R_H$ in CGS units to the value in volt-cm/amp-gauss, multiply by $9 \times 10^{11}$; to convert $R_H$ in CGS to $m^3$/coulomb, multiply by $9 \times 10^{13}$.]

| Metal | Method | Experimental $R_H$, in $10^{-24}$ CGS units | Assumed carriers per atom | Calculated $-1/nec$, in $10^{-24}$ CGS units |
|---|---|---|---|---|
| Li | conv. | −1.89 | 1 electron | −1.48 |
| Na | helicon | −2.619 | 1 electron | −2.603 |
| | conv. | −2.3 | | |
| K | helicon | −4.946 | 1 electron | −4.944 |
| | conv. | −4.7 | | |
| Rb | conv. | −5.6 | 1 electron | −6.04 |
| Cu | conv. | −0.6 | 1 electron | −0.82 |
| Ag | conv. | −1.0 | 1 electron | −1.19 |
| Au | conv. | −0.8 | 1 electron | −1.18 |
| Be | conv. | +2.7 | — | — |
| Mg | conv. | −0.92 | — | — |
| Al | helicon | +1.136 | 1 hole | +1.135 |
| In | helicon | +1.774 | 1 hole | +1.780 |
| As | conv. | +50. | — | — |
| Sb | conv. | −22. | — | — |
| Bi | conv. | −6000. | — | — |

it may be not fair to compare exp. data for hall effect with Drude model and not with FEM.

in the table: FEM $\rightarrow$ $n$ (no. of carriers from valence electrons)

examples:

Na: $R_H = -2.619$ exp.

$= -2.603$ FEM

agreement for s-state electrons

Cu: $R_H = -0.6$ exp

$= -0.82$ FEM

$\Rightarrow$ in d-state electrons $\Rightarrow$ less agreement.

Reason: d-state electrons do participate in $R_H$ but not totally free.

exp.: for Be $R_H = +2.7$

$= -2.7$ for FEM

not shown in table

# GROUND-STATE PROPERTIES OF THE ELECTRON GAS

## ❑ Fermi Temperature: $T_F$:

$$\text{def.}\ T_F = \frac{\varepsilon_F}{k_B} \tag{2.17}$$

$$\because N = \frac{V}{3\pi^2} k_F^{\ 3} \tag{2.12}$$

$$\therefore k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \tag{2.18}$$

$$\therefore \varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \tag{2.19}$$

$$\therefore v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \tag{2.20}$$

$$\therefore T_F = \frac{\hbar^2}{2mk_B}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \tag{2.21}$$

# THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

- *Here: We want to derive the Fermi-Dirac Distribution function*
- When we have *N-paricle system* of electrons at T≠ 0, it will be in a steady state where we can average all properties as:

$$\mathrm{P}_N(E) = \frac{e^{-E/K_BT}}{\sum e^{-E_\alpha{}^{\mathrm{N}}/K_BT}} \qquad (2.22)$$

Where $\mathrm{P_N}$ is the weight function

- In the newminator we do have the Boltzman factor.
- $P_N(E)$: the probabliltiy of the system to be in the state E.
- This formula arises from the postulate that the probability of finding a system in a particular state is proportional to the Boltzmann factor for that state. The partition function in the denominator serves as a normalization factor to ensure that the sum of the probabilities of all possible states is equal to one.

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION*

- Here $E_\alpha^N$ is the energy of the $\alpha$th stationary state of the N-electron system (the sum being over all such states).
- The denominator of (2.22) is called the partition function, and is related to the Helmholtz free energy. *F = U - TS* (where *U* is the internal energy and S, the entropy) by:

$$\sum e^{-E_\alpha{}^N/K_BT} = e^{-F_N/K_BT} \qquad (2.23)$$

$$(2.22) \rightarrow \mathrm{P}_N(E) = e^{-(E-F_N)/K_BT} \qquad (2.24)$$

- We have selected the system to be at T$\neq$ 0, so that thermal fluctuations allow the system to explore different energy states.
- The distribution must be modified to account for the Pauli exclusion principle for Fermions.

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION*

- Let $f_i^N$ represents the probability of finding an electron in the particular one-electron level *i,* when the N-electron system is in thermal equilibrium.

$$f_i^N = \sum \mathrm{P}_N (E_\alpha^N) \qquad (2.25)$$

$$= 1 - \sum \mathrm{P}_N (E_\gamma^N) \qquad (2.26)$$

- Where the last summation is the summation over all N-electron states $\gamma$ in which there is *no* electron in the one-electron level *i*.
- We then do the summation over all (*N + 1*)-electron states in which there is an electron in the one-electron level i:

$$f_i^N = 1 - \sum \mathrm{P}_N (E_\alpha^{N+1} - \varepsilon_i) \qquad (2.27)$$

$$= 1 - \sum e^{(\varepsilon_i - \mu)/K_B T} \, \mathrm{P}_{N+1}\left(E_\alpha^{N+1}\right)$$

$$= 1 - e^{(\varepsilon_i - \mu)/K_B T} \sum \mathrm{P}_{N+1}\left(E_\alpha^{N+1}\right) \qquad (2.28)$$

# THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

- where μ, known as the chemical potential, is given at temperature T by:

$$\mu = F_{N+1} - F_N \qquad (2.29)$$

- Comparing (2.28) with (2.25):

$$f_i^{\,N} = 1 - e^{(\varepsilon_i - \mu)/K_B T} f_i^{\,N+1} \qquad (2.29)$$

- Equation (2.29) gives an exact relation between the probability of the one electron level *i* being occupied at temperature T in an N-electron system, and in an *(N* + 1)-electron system
- For large N, $f_i^{N+1} \approx f_i^N$

$$f_i^{\,N} = 1 - e^{(\varepsilon_i - \mu)/K_B T} f_i^{\,N} \to f_i^{\,N}\left(1 + e^{(\varepsilon_i - \mu)/K_B T}\right) = 1$$

$$\therefore f_i^{\,N} = \frac{1}{e^{(\varepsilon_i - \mu)/K_B T} + 1} \qquad (2.30)$$

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION*

- In reality, no need for the superscript N, Hence: Fermi-Dirac Function can be written as:

$$f_i = \frac{1}{e^{(\varepsilon_i - \mu)/K_B T} + 1} \qquad (2.30)$$

- Total No. of states N is then:

$$N = \sum_i f_i = \sum_i \frac{1}{e^{(\varepsilon_i - \mu)/K_B T} + 1} \qquad (2.31)$$

- Hence, N depends on T and μ

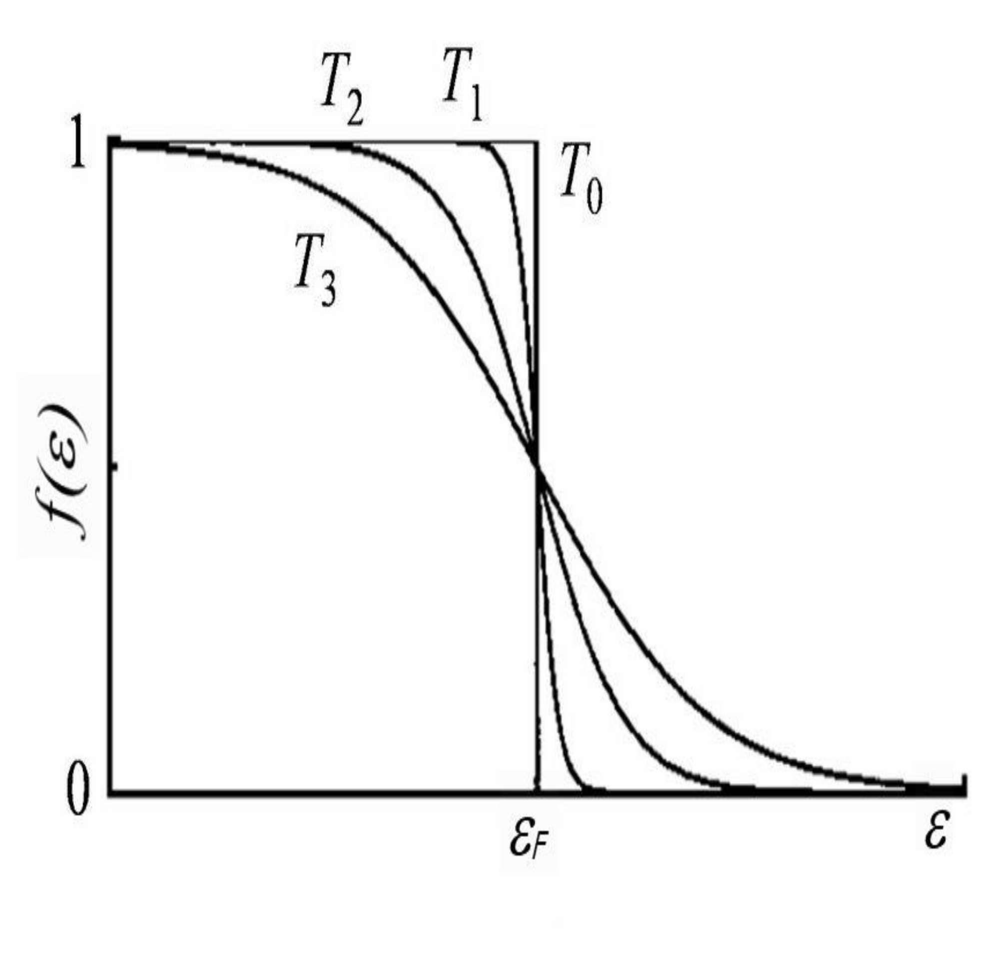
# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

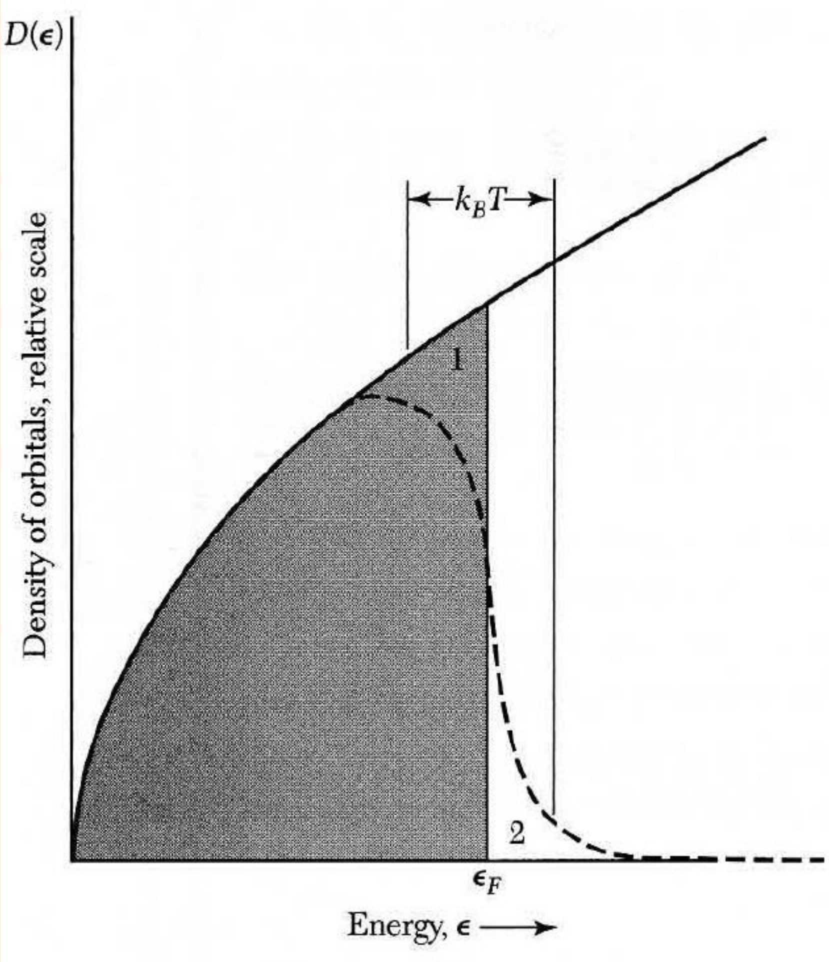
- We are going to derive an equation of the *heat capacity* based on this statistics.
- Classical statistical mechanics predicts that a free particle should have a heat capacity of $\frac{2}{3}k_B$.
- If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $\frac{2}{3}Nk_B$
- But the observed electronic contribution at room temperature is usually less than 0.01% of this value
- This important discrepancy distracted the early workers, such as Lorentz: *How can the electrons participate in electrical conduction processes as if they were mobile, while not contributing to the heat capacity?*

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- The question was answered only upon the discovery of the Pauli exclusion principle and the Fermi distribution function
- Fermi found the correct result and he wrote, "*One recognizes that the specific heat vanishes at absolute zero and that at low temperatures it is proportional to the absolute temperature*."
- When we heat the specimen from 0 K, not every electron gains an energy ~$k_BT$ as expected classically, but only those electrons in orbitals within an energy range $k_BT$ of the Fermi surface are excited thermally.
- This gives an immediate qualitative solution to the problem of the heat capacity of the conduction electron gas.
- If N is the No. of electrons, only a fraction of the order of $T/T_F$ can be excited thermally at $T$, because only these lie within an energy range of the order of $k_BT$ of the top of the energy distribution.

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*



## *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- Each of the $N.T/T_F$ electrons has a thermal energy of the order $k_B T$
- The total electronic thermal kinetic energy $U$ is of the order of:

$$U_{el} \approx \frac{NT}{T_F} k_B T \qquad (2.32)$$

$$\rightarrow C_{el} = \frac{\partial U_{el}}{\partial T} \approx N k_B \left(\frac{T}{T_F}\right) \qquad (2.33)$$

- So, it is directly proportional to $T$, in agreement with the experimental results.
- We now derive a quantitative expression for the electronic heat capacity valid at low temperatures: $k_B T \ll \varepsilon_F$
- The increase $\Delta U = U(T) - U(0)$ in the total energy of a system of $N$ electrons when heated from 0 to $T$ is:

$$\Delta U = \int_0^\infty \varepsilon d\varepsilon D(\varepsilon) f(\varepsilon) - \int_0^{\varepsilon_F} \varepsilon d\varepsilon D(\varepsilon) \qquad (2.34)$$

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- f(ε) is the Fermi-Dirac distribution function showed before. And D(ε) is the number of orbitals per unit energy range.

$$f(\varepsilon, T, \mu) = \frac{1}{e^{(\varepsilon-\mu)/K_B T} + 1} \qquad (2.30)$$

$$\because N = \int_0^\infty d\varepsilon D(\varepsilon) f(\varepsilon) = \int_0^{\varepsilon_F} d\varepsilon D(\varepsilon) \qquad (2.35)$$

N is the total no. of electrons.

$(2.35) \times \varepsilon_F$ :

$$\int_0^\infty \varepsilon_F d\varepsilon D(\varepsilon) f(\varepsilon) = \int_0^{\varepsilon_F} \varepsilon_F d\varepsilon D(\varepsilon)$$

$$\rightarrow \int_0^{\varepsilon_F} \int_{\varepsilon_F}^\infty \varepsilon_F d\varepsilon D(\varepsilon) f(\varepsilon) = \int_0^{\varepsilon_F} \varepsilon_F d\varepsilon D(\varepsilon) \qquad (2.36)$$

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- Using (2.36) in (2.34):

$$\Delta U = \int_{\varepsilon_F}^{\infty} d\varepsilon(\varepsilon-\varepsilon_F)D(\varepsilon)f(\varepsilon) + \int_{0}^{\infty} d\varepsilon(\varepsilon_F-\varepsilon)\left[1-f(\varepsilon)\right]D(\varepsilon) \qquad (2.37)$$

- The first integral on the right-hand side of (2.37) gives the energy needed to take electrons from $\varepsilon_F$ to the orbitals of energy $\varepsilon>\varepsilon_F$, and the second integral gives the energy needed to bring the electrons to $\varepsilon_F$ from orbitals below $\varepsilon_F$ .Both contributions to the energy are positive.
- The product $f(\varepsilon)D(\varepsilon)d\varepsilon$ in the first integral of (2.37) is the No. of electrons elevated to orbitals in the energy range $d\varepsilon$ at an energy $\varepsilon$
- The factor [1 - $f(\varepsilon)$] in the second integral is the probability that an electron has been removed from an orbital $\varepsilon$.

The total Change of Energy (Internal):

$\Delta U =$ ① contribution from electrons above $\epsilon_F$

② " " holes below $\epsilon_F$

$$\text{"}\Delta U = \int_{\epsilon_F}^{\infty} d\epsilon \, \underbrace{(\epsilon - \epsilon_F)}_{\text{energy increase of electrons above } \epsilon_F} \, \underbrace{D(\epsilon)}_{\text{Density of states}} \, \underbrace{f(\epsilon)}_{\text{Fermi-D. D.}} + \int_{0}^{\infty} d\epsilon \, \underbrace{(\epsilon_F - \epsilon)}_{\text{energy deficit due to empty states (holes) below } \epsilon_F} [1 - f(\epsilon)] D(\epsilon) \quad ①$$

Now: at $T = 0$ all states below $\epsilon_F$ : Full

" " above " : vacant

at $T > 0$ some of electrons below $\epsilon_F$ move above $\epsilon_F$ $\Longrightarrow$ vacant states below $\epsilon_F$

$\Longrightarrow$ holes

in $1^{st}$ integral: $f(\epsilon) D(\epsilon) d\epsilon$ = No. of electrons Elevated to orbitals in the Energy Range $d\epsilon$

in $2^{nd}$ " : $[1 - f(\epsilon)]$ is the Probability that e has been removed from orbital $\epsilon$.

orbital ≡ Dot (Point)

Now: we need to find $C_{el} = \frac{dU}{dT}$ ... (2)

⇒ we need to take $\frac{d}{dT}$ for (1)

$C_{el} = \frac{d}{dT}(1)$

we will split the integrand in Integration (2)

$$\Delta U = \int_{\epsilon_F}^{\infty} d\epsilon\,(\epsilon-\epsilon_F)\, f(\epsilon)\, D(\epsilon)$$

$$-\underbrace{\int_{0}^{\infty} \epsilon\, D(\epsilon)\, d\epsilon + \int_{0}^{\infty} \epsilon_F\, D(\epsilon)\, d\epsilon}_{=0} + \int_{0}^{\infty} (\epsilon-\epsilon_F)\, f(\epsilon)\, D(\epsilon)\, d\epsilon \quad \text{---} \; (3)$$

$$\Delta U = \int_{\epsilon_F}^{\infty} (\epsilon-\epsilon_F)\, f(\epsilon)\, D(\epsilon)\, d\epsilon + \int_{0}^{\infty} (\epsilon-\epsilon_F)\, f(\epsilon)\, D(\epsilon)\, d\epsilon \quad \text{---} \; (4)$$

2nd Integral includes First Integral $\int_0^\infty$

$$\therefore \; \Delta U = \int_{0}^{\infty} (\epsilon-\epsilon_F)\, f(\epsilon)\, D(\epsilon)\, d\epsilon \quad \text{------} \; (5)$$

$$\therefore \; C_{el} = \frac{d}{dT} \int_{0}^{\infty} (\epsilon-\epsilon_F)\, f(\epsilon)\, D(\epsilon)\, d\epsilon \quad \text{--} \; (6)$$

$$\because \; C_{el} = \int_0^\infty (\epsilon - \epsilon_F) \frac{\partial f(\epsilon)}{\partial T} D(\epsilon)\, d\epsilon \quad \text{----} \; (7) \quad (2.38)$$

let $D(\epsilon) \approx D(\epsilon_F)$

$$(7) \Rightarrow C_{el} = D(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{\partial f(\epsilon)}{\partial T} d\epsilon \quad \text{----} \; (8)$$

$$\because \; K_B T << \epsilon_F \longrightarrow \mu \approx \epsilon_F \quad \text{----} \; (9)$$

$$\frac{\partial f(\epsilon)}{\partial T} = \frac{\partial}{\partial T} \frac{1}{e^{(\epsilon - \epsilon_F)/K_B T} + 1}$$

$$= K_B \frac{(\epsilon - \epsilon_F)}{(K_B T)^2} \frac{e^{(\epsilon - \epsilon_F)/K_B T}}{\left[ e^{(\epsilon - \epsilon_F)/K_B T} + 1 \right]^2} \quad \text{----} \; (10)$$

let $\dfrac{\epsilon - \epsilon_F}{K_B T} = x \Rightarrow d\epsilon = K_B T\, dx$

$$\Rightarrow \epsilon = x K_B T - \epsilon_F$$

$$\text{at } \epsilon = 0 \Rightarrow x = \frac{\epsilon_F}{K_B T} \qquad \text{at } \epsilon = \infty \Rightarrow x = \infty$$

$$(8) \Rightarrow C_{el} = \frac{D(\epsilon_F)}{(K_B T)^2} K_B \int_0^\infty (\epsilon - \epsilon_F)^2 \frac{e^{\frac{\epsilon - \epsilon_F}{K_B T}}}{\left[e^{\frac{\epsilon - \epsilon_F}{K_B T}} + 1\right]^2} d\epsilon \qquad (11)$$

$$\Rightarrow C_{el} = \frac{K_B D(\epsilon_F)}{\cancel{(K_B T)^2}} \int_{-\frac{\epsilon_F}{K_B T}}^{\infty} \cancel{(K_B T)^2} x^2 \frac{e^x}{(e^x+1)^2} (K_B T) dx$$

$$\Rightarrow C_{el} = K_B^2 T D(\epsilon_F) \int_{-\frac{\epsilon_F}{K_B T}}^{\infty} x^2 \frac{e^x}{(e^x+1)^2} dx \quad \text{--} (12)$$

$$\because \int_{-\infty}^{+\infty} \frac{x^2 e^x}{(e^x+1)^2}\, dx = \frac{\pi^2}{3} \quad \text{---} \quad (13)$$

$$\therefore C_{el} = \frac{\pi^2}{3} \cdot k_B^2 \cdot T\, D(\epsilon_F) \quad \text{---} \quad (14)$$

this is similar to eq (2-84)
in Ashroft (Page 49).

you can stop here.
or work in more simple and expression
form.

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

$$\because \ D(\epsilon) = \frac{dN}{d\epsilon} = \frac{\cancel{3}}{2}\cdot\frac{V}{\cancel{3}\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}$$

$$= \frac{1}{2}\frac{V}{\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}\frac{\epsilon^{1/2}}{\epsilon^{3/2}} \quad \cdots - (16)$$

$$\therefore \ D(\epsilon) = \frac{3}{2}\left[\frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}\right]\cdot\frac{1}{\epsilon}$$

$$= \frac{3}{2}\frac{1}{\epsilon}N$$

$$\therefore \ D(\epsilon_F) = \frac{3}{2}\frac{N}{K_B T_F}$$

$$\therefore \ C_{el} = \frac{\pi^2}{3}\cdot K_B^2 T\, D(\epsilon_F)$$

$$= \frac{\pi^2}{\cancel{3}} K_B^{\cancel{2}} T \cdot \frac{\cancel{3}}{2} \frac{N}{\cancel{K_B} T_F}$$

$$\therefore \boxed{C_{el} = \frac{1}{2} \pi^2 \left(\frac{T}{T_F}\right) \cdot N K_B} \quad \cdots (17)$$

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- The heat capacity is found on differentiating $\Delta U$ with respect to $T$. The only temperature-dependent term in (2.37) is $f(\varepsilon)$

$$C_{el} = \frac{dU}{dT} = \frac{d}{dT}\left[\int_{\varepsilon_F}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon - \int_0^{\infty}(\varepsilon-\varepsilon_F)\left[1-f(\varepsilon)\right]D(\varepsilon)d\varepsilon\right]$$

$$= \frac{d}{dT}\left[\int_{\varepsilon_F}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon - \int_0^{\infty}\varepsilon D(\varepsilon)d\varepsilon + \int_0^{\infty}\varepsilon_F D(\varepsilon)d\varepsilon + \int_0^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon\right]$$

$$= \frac{d}{dT}\left[\int_{\varepsilon_F}^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon + \int_0^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon\right]$$

$$= \frac{d}{dT}\left[\int_0^{\infty}(\varepsilon-\varepsilon_F)f(\varepsilon)D(\varepsilon)d\varepsilon\right]$$

$$C_{el} = \left[\int_0^{\infty}(\varepsilon-\varepsilon_F)\frac{\partial f(\varepsilon)}{\partial T}D(\varepsilon)d\varepsilon\right] \tag{2.38}$$

# THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION

## ❑ By approximating $D(\varepsilon) \approx D(\varepsilon_F)$:

$$C_{el} \approx D(\varepsilon_F)\int_0^{\infty}(\varepsilon-\varepsilon_F)\frac{\partial f(\varepsilon)}{\partial T}d\varepsilon \qquad (2.39)$$

$$\because k_B T << \varepsilon_F \rightarrow \mu \approx \varepsilon_F$$

$$\therefore \frac{\partial f(\varepsilon)}{\partial T} = \frac{\partial}{\partial T}\frac{1}{e^{(\varepsilon-\varepsilon_F)/K_B T}+1}$$

$$= k_B \frac{(\varepsilon-\varepsilon_F)}{\left(k_B T\right)^2}\frac{e^{(\varepsilon-\varepsilon_F)/K_B T}}{\left[e^{(\varepsilon-\varepsilon_F)/K_B T}+1\right]^2} \qquad (2.40)$$

$$\text{let}: x = \frac{\varepsilon-\varepsilon_F}{k_B T} \qquad (2.41)$$

$$\therefore C_{el} = k_B^2 T D(\varepsilon_F)\int_{-\frac{\varepsilon_F}{K_B T}}^{\infty} x^2 \frac{e^x}{\left(e^x+1\right)^2}dx \qquad (2.42)$$

# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- We may replace the lower limit by $-\infty$ because the factor $e^x$ in the integrand is already negligible at $x = -\varepsilon_F/k_BT$

$$\int_{-\infty}^{\infty} x^2 \frac{e^x}{\left(e^x+1\right)^2} dx = \frac{\pi^2}{3} \qquad (2.43)$$

$$\therefore C_{el} = \frac{1}{3}\pi^2 D(\varepsilon_F)\,\mathrm{k}_B^2\, T \qquad (2.44)$$

$$\varepsilon = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad (2.19) \Rightarrow N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}$$

$$\because D(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{3}{2}.\frac{V}{3\pi^2}.\left(\frac{2m}{\hbar^2}\right)^{3/2}(\varepsilon)^{1/2} = \frac{3}{2}.\frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}.\frac{\varepsilon^{1/2}}{\varepsilon^{3/2}}$$

$$\therefore D(\varepsilon) = \frac{3}{2}\frac{N}{\varepsilon} = \frac{3}{2}\frac{N}{K_B T_F}$$

$$\therefore C_{el} = \frac{1}{2}\left(\pi^2 \frac{T}{T_F}\right) N k_B \qquad (2.44)$$

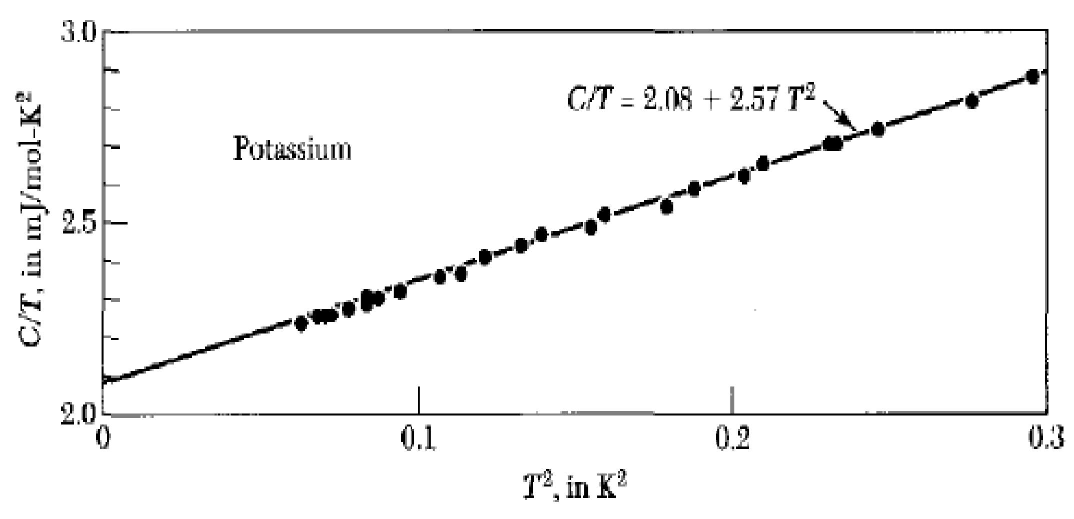
# *THERMAL PROPERTIES OF THE FREE ELECTRON GAS: Applications of THE FERMI-DIRAC DISTRIBUTION*

- Hence, $C_{el}$ or $C_v$ is linear in T.
- The prediction of a linear specific heat is one of the most important consequences of Fermi-Dirac statistics. The general form of heat capacity is:

$$C_v = \gamma T + AT^3 \tag{2.45}$$

$$\therefore \frac{C_v}{T} = \gamma + AT^2 \tag{2.46}$$

One can thus find γ by extrapolating the C/T curve linearly down to $T^2 = 0$, and noting where it intercepts the C/T -axis



# The Sommerfeld Theory of Metals

SOME ROUGH EXPERIMENTAL VALUES FOR THE COEFFICIENT OF THE LINEAR TERM IN $T$ OF THE MOLAR SPECIFIC HEATS OF METALS, AND THE VALUES GIVEN BY SIMPLE FREE ELECTRON THEORY

| ELEMENT | FREE ELECTRON $\gamma$ (in $10^{-4}$ cal-mole$^{-1}$-K$^{-2}$) | MEASURED $\gamma$ (in $10^{-4}$ cal-mole$^{-1}$-K$^{-2}$) | RATIO[a] ($m^*/m$) |
|---|---|---|---|
| Li | 1.8 | 4.2 | 2.3 |
| Na | 2.6 | 3.5 | 1.3 |
| K | 4.0 | 4.7 | 1.2 |
| Rb | 4.6 | 5.8 | 1.3 |
| Cs | 5.3 | 7.7 | 1.5 |
| Cu | 1.2 | 1.6 | 1.3 |
| Ag | 1.5 | 1.6 | 1.1 |
| Au | 1.5 | 1.6 | 1.1 |
| Be | 1.2 | 0.5 | 0.42 |
| Mg | 2.4 | 3.2 | 1.3 |
| Ca | 3.6 | 6.5 | 1.8 |
| Sr | 4.3 | 8.7 | 2.0 |
| Ba | 4.7 | 6.5 | 1.4 |
| Nb | 1.6 | 20 | 12 |
| Fe | 1.5 | 12 | 8.0 |
| Mn | 1.5 | 40 | 27 |
| Zn | 1.8 | 1.4 | 0.78 |
| Cd | 2.3 | 1.7 | 0.74 |
| Hg | 2.4 | 5.0 | 2.1 |
| Al | 2.2 | 3.0 | 1.4 |
| Ga | 2.4 | 1.5 | 0.62 |
| In | 2.9 | 4.3 | 1.5 |
| Tl | 3.1 | 3.5 | 1.1 |
| Sn | 3.3 | 4.4 | 1.3 |
| Pb | 3.6 | 7.0 | 1.9 |
| Bi | 4.3 | 0.2 | 0.047 |
| Sb | 3.9 | 1.5 | 0.38 |

# The Sommerfeld Theory of Metals

from the table; we notice the big difference for Nb and Mn

this is a failure in FEM

Why?

FEM:

1. ignores strong Electron Correlations
2. it " e-e interaction
   → large Density of State at $E_F$
3. ignores d-electron Contribution
4. it ignores any magnetic effects

these effects are strong in Nb and Mn

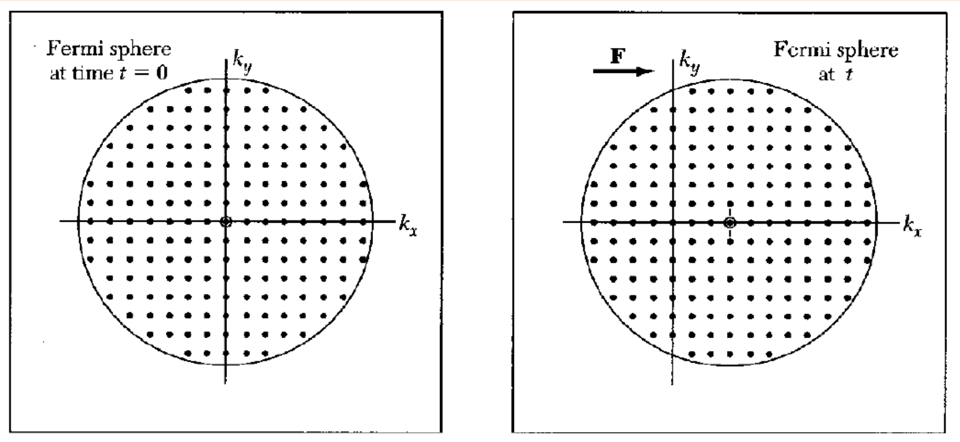
# *Sommerfeld Theory of Conduction in Metals*

- To find the velocity distribution for electrons in metals, consider a small volume element of k-space about a point **k,** of volume *d***k**
- The number of one-electron levels in this volume element is (from 2.10) with the twofold spin degeneracy in consideration:

$$\left(\frac{V}{4\pi^3}\right)d\mathbf{k} \qquad (2.47)$$

- The probability of each level being occupied is just *f(ε)*
- therefore the total number of electrons in the k-space volume element is:

$$\left(\frac{V}{4\pi^3}\right)f\ (\varepsilon)d\mathbf{k} \qquad (2.48)$$




(a) (b)

# *Sommerfeld Theory of Conduction in Metals*

- The velocity of a free electron with wave vector **k** is $\boldsymbol{v} = \hbar\boldsymbol{k}/m$
- the number of electrons in an element of volume dV about $\boldsymbol{v}$ is the same as the number in an element of volume: $d\boldsymbol{k} = (m/\hbar)^3 d\boldsymbol{v}$
- Consequently the total number of electrons per unit volume of real space in a velocity space element of volume dV about $\boldsymbol{v}$ is: $f(\boldsymbol{v})d\boldsymbol{v}$ with:

$$f(v) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{\exp\left[\left(\frac{1}{2}mv^2 - \mu\right)/k_B T\right] + 1} \qquad (2.49)$$

- Sommerfeld reexamined the Drude model, replacing the classical Maxwell-Boltzmann velocity distribution (2.1) by the Fermi-Dirac distribution (2.49).

# *Sommerfeld Theory of Conduction in Metals*

❑ Fermi velocity can be derived as:

$$\because v = \frac{\hbar k}{m}$$

$$\therefore v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad (2.50)$$

$$\because \ell = v_F \tau$$

$$\therefore \ell = \frac{\hbar \tau}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad (2.50)$$

❑ This is the mean free path of electrons

# Thanks