6.11 Derive the Planck radiation formula for a two-dimensional space and hence deduce the Stefan–Boltzmann law.

6.12 Obtain the mean energy of a harmonic oscillator on the basis of quantum statistics. Hence discuss the Debye formula for the specific heat of a solid at low temperature.

6.13 Show that at low temperatures, the specific heat of solid can be expressed in the form

$$C_v = aT + bT^3$$

Discuss how far it agrees with experimental results.

6.14 Deduce the partition function for a Debye model of solid. Show that at low temperatures, the specific heat of such a solid should vary as $T^3$.

6.15 Derive the Debye formula for the specific heat of a two-dimensional system at low temperatures.

6.16 Show that the specific heat at low temperature for n-dimensional solid-body obeys the law $C_v \sim T^n$. 
7.1 IDEAL FERMI GAS: WEAKLY DEGENERATE

We consider an ideal Fermi gas, which obeys Fermi-Dirac statistics. For such a gas, the total number of particles and the total energy are given by

\[ N = \sum_i n_i = \int_0^\infty \frac{g(\epsilon)}{z^{-1} e^{\beta \epsilon} + 1} \, d\epsilon \]  
(7.1)

\[ U = \sum_i \epsilon_i n_i = \int_0^\infty \frac{\epsilon g(\epsilon)}{z^{-1} e^{\beta \epsilon} + 1} \, d\epsilon \]  
(7.2)

where \( \beta = (kT)^{-1} \) and \( z = e^{\beta \epsilon} \). In this case, the particles will be distributed among the various quantum states, so that no more than one particle can be in each quantum state (Pauli's exclusion principle).

As derived in Sec. 6.1, the number of quantum states with energy \( \epsilon \) and \( \epsilon + d\epsilon \) is given by

\[ g(\epsilon) \, d\epsilon = \frac{2\pi gV}{h^3} (2m)^{3/2} \epsilon^{1/2} \, d\epsilon \]  
(7.3)

Using this value of \( g(\epsilon) \, d\epsilon \) in Eqs. (7.1) and (7.2), we get

\[ N = \frac{2\pi gV}{h^3} (2m)^{3/2} F_{3/2}(z) \]  
(7.4)

\[ U = \frac{2\pi gV}{h^3} (2m)^{3/2} F_{3/2}(z) \]  
(7.5)

where

\[ F_n(z) = \int_0^\infty \frac{\epsilon^{(n-1)}}{z^{-1} e^{\beta \epsilon} + 1} \, d\epsilon \]  
(7.6)

Putting \( \beta \epsilon = X \), the function \( F_n(z) \) can be written in the form

\[ F_n(z) = (kT)^n \int_0^\infty \frac{X^{n-1}}{z^{-1} e^X + 1} \, dX \]

\[ = (kT)^n \Gamma(n) f_n(z) \]  
(7.7)
where
\[ f_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{X^{n-1}}{z^{-1} e^X + 1} dX \] (7.8)

and \( \Gamma(n) \) is the Gamma function. Then, we get
\[ N = \frac{gV}{\lambda^3} f_{3/2}(z) \] (7.9)
\[ U = \frac{3}{2} kT \frac{gV}{\lambda^3} f_{3/2}(z) \] (7.10)

where
\[ \lambda = (\hbar^2/(2mkT))^{1/2} \] (7.11)

is the thermal wavelength.

When \( z \) is small, \((z^{-1} e^X + 1)^{-1}\) can be expanded in the form
\[ \frac{1}{z^{-1} e^X + 1} = z e^{-X(1 + ze)^{-1}} \]
\[ = \sum_{l=1}^\infty (-1)^{l-1} \frac{z^l}{e^{-lX}} \]

and hence \( f_n(z) \) can be evaluated as
\[ f_n(z) = \frac{1}{\Gamma(n)} \sum_{l=1}^\infty (-1)^{l-1} \frac{z^l}{l^n} \]
\[ = z - \frac{z^2}{2^n} + \frac{z^3}{3^n} - \frac{z^4}{4^n} + \ldots \] (7.12)

In order to determine the thermodynamic properties of the Fermi gas, we must know the fugacity \( z \) as a function of the particle density \( \rho (=N/V) \) and temperature \( T \). From Eq. (7.9)
\[ f_{3/2}(z) = \left( \frac{\rho \lambda^3}{g} \right) = \frac{\rho}{g} \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \] (7.13)

Now in the case of very low density and high temperature, where
\[ f_{3/2}(z) = \frac{\rho}{g} \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \ll 1 \] (7.14)

the gas is said to be highly nondegenerate. From (7.2), this condition implies that \( z \ll 1 \) and hence
\[ f_n(z) = z \]
Then, Eqs (7.9) and (7.10) reduce to

\[ N = \frac{gVz}{\lambda^3} \]  
(7.15)

\[ U = \frac{3}{2} kT \frac{gVz}{\lambda^3} = \frac{3}{2} NkT \]  
(7.16)

Equation (7.16) is the standard result for an ideal classical gas.

If \( z \) is small in comparison to unity but not very small, we use Eq. (7.12). From (7.9) and (7.10), we get

\[ U = \frac{3}{2} NkT \frac{f_{3/2}(z)}{f_{3/2}(z)} \]  
(7.17)

Now it can be shown that

\[ \frac{f_{3/2}(z)}{f_{3/2}(z)} = 1 + \frac{1}{2^{5/2}} f_{3/2}(\frac{z}{2}) - \left( \frac{2}{3^{3/2}} - \frac{1}{2^3} \right) \left( f_{3/2}(z) \right)^2 + \ldots \]

\[ = 1 + \frac{1}{2^{5/2}} \left( \frac{N\lambda^3}{Vg} \right) - \left( \frac{2}{3^{3/2}} - \frac{1}{2^3} \right) \left( \frac{N\lambda^3}{Vg} \right)^2 + \ldots \]  
(7.18)

Then

\[ U = \frac{3}{2} NkT \left[ 1 + \frac{1}{2^{5/2}} \left( \frac{N\lambda^3}{Vg} \right) - \left( \frac{2}{3^{3/2}} - \frac{1}{2^3} \right) \left( \frac{N\lambda^3}{Vg} \right)^2 + \ldots \right] \]  
(7.19)

and the specific heat is

\[ C_V = \frac{3}{2} Nk \left[ 1 - \frac{1}{2^{7/2}} \left( \frac{N\lambda^3}{Vg} \right) + 2 \left( \frac{2}{3^{3/2}} - \frac{1}{2^3} \right) \left( \frac{N\lambda^3}{Vg} \right)^2 + \ldots \right] \]  
(7.20)

The first term of Eqs. (7.19) and (7.20) are, respectively, the energy and specific heat in the Boltzmann limit and the second and third term give the first and second order correction due to the deviation from the classical behaviour.

Using the relation

\[ PV = \frac{2}{3} U \]  
(7.21)

one can obtain the equation of state in the form of the virial expansion:

\[ PV = \frac{1}{3} NkT \left[ 1 + \frac{1}{2^{5/2}} \left( \frac{\rho\lambda^3}{g} \right) - \left( \frac{2}{3^{3/2}} - \frac{1}{2^3} \right) \left( \frac{\rho\lambda^3}{g} \right)^2 + \ldots \right] \]  
(7.22)

The correction terms depend on the value of the quantity \( \rho\lambda^3/g \). The correction term will be small, when

\[ \frac{N}{Vg} \left( \frac{\hbar^2}{2\pi mkT} \right)^{3/2} \ll 1 \]

For this, the gas should be sufficiently rarefied or the temperature \( T \) should be high. At very high temperatures, the correction terms will be very small
and may be neglected, leading to the classical properties. Thus we see that
the deviation from the classical behaviour occurs when the temperature is
lowered at constant density. The deviations in this case cause an increase in
pressure and energy but a decrease in specific heat.

When the temperature and density are such that \((\rho \lambda^3/g)\) is of the order of
unity, the gas is said to become degenerate, and this expansion formalism
cannot be of much use.

7.2 IDEAL FERMI GAS: STRONGLY DEGENERATE

At sufficiently low temperature, \((\rho \lambda^3/g) \gg 1\), and the gas becomes dege-
nerate. When \((\rho \lambda^3/g) \to \infty\), which corresponds to \(T = 0\), the gas is com-
pletely degenerate.

Let us consider a Fermi gas in a degenerate state \((N \lambda^3/Vg \gg 1)\). The
mean occupation number of the single particle state \(\epsilon\) is

\[
\langle n_\epsilon \rangle = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}
\]  

(7.23)

where \(\mu\) is the chemical potential, which is a function of \(T\), i.e. \(\mu = \mu(T)\).
The number of quantum states with the translational motion of a particle
in the energy range \(\epsilon\) and \(\epsilon + d\epsilon\) is given by (7.3), i.e.

\[
g(\epsilon) \, d\epsilon = \frac{2\pi g V}{h^3} (2m)^{3/2} \epsilon^{1/2} \, d\epsilon
\]  

(7.24)

Combining Eqs (7.23) and (7.24), the number of particles in the energy
range \(\epsilon\) and \(\epsilon + d\epsilon\) is given by

\[
n(\epsilon) \, d\epsilon = \frac{g(\epsilon) \, d\epsilon}{e^{(\epsilon - \mu)/kT} + 1}
\]

\[
= \frac{2\pi g V}{h^3} (2m)^{3/2} \frac{\epsilon^{1/2} \, d\epsilon}{e^{(\epsilon - \mu)/kT} + 1}
\]  

(7.25)

The total number of particles in the gas is obtained by integrating
Eq. (7.25) in the limit \(\epsilon = 0\) and \(\epsilon = \infty\):

\[
N = \frac{2\pi g V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2} \, d\epsilon}{e^{(\epsilon - \mu)/kT} + 1}
\]  

(7.26)

The total energy of the gas is

\[
U = \frac{2\pi g V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} \, d\epsilon}{e^{(\epsilon - \mu)/kT} + 1}
\]  

(7.27)

For simplicity, we first consider a Fermi gas in a state of complete dege-
neracy. In the limit \(T \to 0\), where \(\mu \to \mu(0) \equiv \mu_0\), the mean occupation num-
ber becomes

\[
\langle n_\epsilon \rangle = \begin{cases} 
1 & \text{for } \epsilon < \mu_0 \\
0 & \text{for } \epsilon > \mu_0
\end{cases}
\]  

(7.28)
The limiting chemical potential $\mu_0$ is called the Fermi energy $\epsilon_F$ of the system. The variation of $\langle n_\epsilon \rangle$ at absolute zero temperature is shown by a continuous curve in Fig. 7.1. Thus at $T = 0$, all single particle states up to $\epsilon = \epsilon_F$ are completely filled with one particle in each state according to Pauli’s exclusion principle. On the other hand, all single particle states with $\epsilon > \epsilon_F$ are empty. Thus, the Fermi energy $\epsilon_F$ has a physical meaning. It is the energy of the topmost occupied level at $T = 0$. Such a behaviour cannot be shown in case of Bose gas.

![Fig. 7.1](image)

**Fig. 7.1** Fermi-Dirac mean occupation number $\langle n_\epsilon \rangle$ as a function of $\epsilon$: (a) at $T = 0$ represented by solid line (b) at $T > 0$ represented by dashed line.

The energy distribution of the Fermi gas is given by Eq. (7.25). Figure 7.2 shows this distribution at $T = 0$. The sharp cut-off at $\epsilon = \epsilon_F$ shows the behaviour of $\langle n_\epsilon \rangle$.

Using Eq. (7.28) at $T = 0$, Eq. (7.26) reduces to

\[
N = \frac{2\pi g V}{h^3} (2m)^{3/2} \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon
\]

\[
= \frac{4\pi g V}{3h^3} (2m)^{3/2} \epsilon_F^{3/2}
\]

so that the Fermi energy $\epsilon_F$ is

\[
\epsilon_F = \left( \frac{3N}{4\pi g V} \right)^{2/3} \left( \frac{h^2}{2m} \right)
\]

\[
= \left( \frac{3\rho}{4\pi g} \right)^{2/3} \left( \frac{h^2}{2m} \right)
\]

(7.29)

where $\rho = \frac{N}{V}$ is the particle density. Thus the Fermi energy $\epsilon_F$ depends on the particle density $\rho$ and on the mass $m$ of the particle. The Fermi
temperature $T_F$ is defined by

$$
\epsilon_F = kT_F
$$

(7.31)

Substituting Eq. (7.28) in Eq. (7.27) the total ground state energy of the gas is given by

$$
U_0 = \frac{2\pi g V}{\hbar^3} (2m)^{3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon
$$

$$
= \frac{4\pi g V}{5\hbar^3} (2m)^{3/2} \epsilon_F^{5/2}
$$

(7.32)

From (7.29) and (7.32), we get

$$
\frac{U_0}{N} = \frac{3}{5} \epsilon_F
$$

(7.33)

Thus, the average energy per particle of the Fermi gas at $T = 0$ is $3/5$ times the Fermi energy $\epsilon_F$.

Finally the ground state equation of state of the gas at $T = 0$ is

$$
P_0 = \frac{2}{3} \left( \frac{U_0}{V} \right) = \frac{2}{5} \left( \frac{N\epsilon_F}{V} \right)
$$

$$
= \frac{2}{5} \rho \epsilon_F
$$

(7.34)

or substituting the value of $\epsilon_F$

$$
P_0 = \frac{2}{5} \left( \frac{3}{4\pi g} \right)^{2/3} \left( \frac{\hbar^2}{2m} \right)^{5/3} \rho^{5/3}
$$

(7.35)
i.e. \[ P_0 \propto \rho^{5/3} \] (7.36)

Thus the pressure of a Fermi gas at \( T = 0 \) is proportional to the \((5/3)\) power of the density.

So far we have considered a Fermi gas at zero temperature. Now we consider it at finite temperature. At \( T \ll T_F \), the mean occupation number \( \langle n_e \rangle \) and energy distribution \( n(\epsilon) \) are very similar to those at \( T = 0 \), shown in Figs. 7.1 and 7.2. Such a gas is called extremely degenerate. The mean occupation number \( \langle n_e \rangle \) and energy distribution at \( T < T_F \) are shown by dashed lines in Figs. 7.1 and 7.2. The solid lines correspond to curves for \( T = 0 \). As the temperature \( T \) is raised from \( T = 0 \), the particles are excited from single particle states with energy \( \epsilon < \epsilon_F \) to single particle states with energy \( \epsilon > \epsilon_F \). This transition is only in a narrow range of the value of the energy \( \epsilon \), close to the Fermi energy \( \epsilon_F \). The width of this transition zone of the Fermi distribution is of the order of \( kT \). The major part of the system remains unaffected by the rise in temperature; only a fraction of the particles is in the thermally excited states.

For a study of a Fermi gas at finite but low temperature, where \( z > 1 \), we take Eqs. (7.26) and (7.27) for the total number of particles and total energy of the system, which can be expressed as [see Eqs. (7.4) and (7.5)]

\[ N = \frac{2\pi g V}{h^3} (2m)^{3/2} F_{5/2}(z) \] (7.37)

\[ U = \frac{2\pi g V}{h^3} (2m)^{3/2} F_{5/2}(z) \] (7.38)

where

\[ F_n(z) = \int_0^\infty \frac{e^{n-1} d\epsilon}{e^{(\epsilon-\mu)/kT} + 1} \] (7.39)

In order to solve the integral of (7.39) when \( z \) is large \((z > 1)\), we put \((\epsilon - \mu)/kT = X\), then

\[ F_n(z) = kT \int_{-\mu/kT}^{\mu/kT} \frac{(\mu + kTX)^{n-1}}{e^X + 1} dX \]

\[ = kT \int_0^{\mu/kT} \frac{(\mu - kTX)^{n-1}}{e^{-X} + 1} dX + kT \int_0^\infty \frac{(\mu + kTX)^{n-1}}{e^X + 1} dX \]

Using the relation

\[ \frac{1}{e^{-X} + 1} = 1 - \frac{1}{e^X + 1} \]
\[ F_n(z) \text{ can be written as} \]
\[ F_n(z) = \int_0^\infty e^{n-1} \, d\varepsilon - kT \int_0^{\mu/kT} \frac{(\mu - kT\varepsilon)^{n-1}}{e^{\mu/kT} + 1} \, d\varepsilon \]
\[ + kT \int_0^\infty \frac{(\mu + kT\varepsilon)^{n-1}}{e^{\mu/kT} + 1} \, d\varepsilon \]
\[ = \frac{k^n}{n} + kT \int_{\mu/kT}^\infty \frac{(\mu + kT\varepsilon)^{n-1} - (\mu - kT\varepsilon)^{n-1}}{e^{\mu/kT} - 1} \, d\varepsilon \]
\[ + kT \int_{\mu/kT}^\infty \frac{1}{e^{\mu/kT} + 1} \, d\varepsilon \]

Since \( \mu/kT \gg 1 \), the contribution of the last integral is very small and can be neglected. Thus after expanding
\[ (\mu \pm kT\varepsilon)^{n-1} = \mu^{n-1} (1 \pm kT\varepsilon/\mu)^{n-1} \]
we obtain
\[ F_n(z) = \mu^n \left[ \frac{1}{n} + 2(n - 1) \left( \frac{kT}{\mu} \right)^2 f_2(1) \right. \]
\[ + \left. \frac{(n - 1)(n - 2)(n - 3)}{3} \left( \frac{kT}{\mu} \right)^4 f_4(1) + \ldots \right] \]
where the function \( f_m(1) \) is defined from (7.8). Thus,
\[ f_m(1) = \sum_{|m| = 1}^\infty (-1)^{l-1} \frac{1}{l^m} \]
\[ = (1 - 2^{1-m})\zeta(m). \]
Here
\[ \zeta(m) = \sum_{l=1}^\infty \frac{1}{l^m} \]
is the Riemann zeta function. Then
\[ f_m(1) = \frac{\pi^2}{12} \quad \text{for } m = 2 \]
\[ = \frac{7\pi^4}{120} \quad \text{for } m = 4 \]
Thus for large \( z_0 \) (i.e. \( z > 1 \)), \( F_n(z) \) can be evaluated as
\[ F_n(z) = \frac{1}{n} \mu^n \left[ 1 + \frac{\pi^2}{6} n(n - 1) \left( \frac{kT}{\mu} \right)^2 \right. \]
\[ + \left. \frac{7\pi^4}{360} n(n - 1)(n - 2)(n - 3) \left( \frac{kT}{\mu} \right)^4 + \ldots \right] \quad (7.40) \]
Comparing (7.29) and (7.37), we get
\[
\mu = \epsilon_F \left[ 1 + \frac{\pi^2}{8} \left( \frac{kT}{\mu} \right)^2 + \frac{7\pi^4}{640} \left( \frac{kT}{\mu} \right)^4 + \ldots \right]^{-2/3}
\]
\[
= \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{kT}{\mu} \right)^2 - \frac{\pi^4}{720} \left( \frac{kT}{\mu} \right)^4 + \ldots \right]
\] (7.41)

This can be solved by the method of iteration. Thus,
\[
\mu \simeq \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 - \frac{\pi^4}{80} \left( \frac{T}{T_F} \right)^4 + \ldots \right]
\] (7.42)

The variation of the chemical potential \( \mu \) of an ideal Fermi gas with the absolute temperature \( T \) is shown in Fig. 7.3. At \( T = 0 \), the chemical potential is equal to the Fermi energy \( \epsilon_F \).

![Fig. 7.3 Variation of the chemical potential \( \mu \) of an ideal Fermi gas as a function of \( T/T_F \)](image)

As the temperature increases, the chemical potential decreases and becomes zero at a temperature, just below the Fermi temperature \( T_F \). As the temperature increases further, the chemical potential becomes more and more negative.

Then with the help of Eqs. (7.29) and (7.42), Eq. (7.38) can be written as
\[
U = \frac{3}{5} N\epsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 - \frac{\pi^4}{16} \left( \frac{T}{T_F} \right)^4 + \ldots \right]
\] (7.43)

The variation of energy \( U \) with \( T \) is shown in Fig. 7.4. For ideal Boltzmann gas, \( U = 3/2 NkT \), which is also demonstrated in the figure. It is evident from the figure that the energy of an ideal Fermi gas is always greater than that of an ideal Boltzmann gas.

Then, specific heat of the gas becomes
\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V
\]
\[
= Nk \left[ \frac{\pi^2}{2} \left( \frac{T}{T_F} \right)^2 - \frac{3\pi^4}{20} \left( \frac{T}{T_F} \right)^3 + \ldots \right]
\] (7.44)
Thus for $T < T_F$, the specific heat of the degenerate Fermi gas varies as

$$C_V = aT + bT^3$$  \hspace{1cm} (7.45)

when

$$T \ll T_F$$

$$C_V = aT$$  \hspace{1cm} (7.46)

Thus, as $T \to 0$, $C_V \to 0$. The variation of $C_V$ with $T$ is shown in Fig. 7.5. It is considerably smaller than the classical value $3/2 Nk$.

The pressure of the gas is then given by

$$P = \frac{2}{3} \left( \frac{U}{V} \right) = \frac{2}{5} \frac{N\varepsilon_F}{V} \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 - \frac{\pi^4}{16} \left( \frac{T}{T_F} \right)^4 + \ldots \right]$$  \hspace{1cm} (7.47)
The first terms of (7.43) and (7.47) are the ground state values and other terms are corrections arising due to the rise of temperature.

From (7.42) and (7.47), the Helmholtz free energy of the degenerate Fermi gas is

\[ A = \mu N - PV \]

\[ = N\epsilon_F \left[ 1 - \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \frac{\pi^2}{48} \left( \frac{T}{T_F} \right)^4 + \ldots \right] \]  \hspace{1cm} (7.48)

and hence entropy of system is

\[ S = Nk \left[ \frac{\pi^2}{2} \left( \frac{T}{T_F} \right) - \frac{\pi^4}{20} \left( \frac{T}{T_F} \right)^3 + \ldots \right] \]  \hspace{1cm} (7.49)

From this, it is clear that \( S \to 0 \) when \( T \to 0 \) in accordance with the third law of thermodynamics.

From the study of degenerate Fermi gas, we conclude that \( C_F \) and \( S \) vanish at absolute zero whereas \( U \) and \( P \) remain finite.

### 7.3 FREE ELECTRON THEORY OF METALS

In metals, the electrons in the outermost shells of the atoms are weakly bound. These electrons become detached, and move freely through the volume of the metal. They are conductors of electricity and many properties of the metals are determined by the motion of these conduction electrons. This is the free electron model. In a solid metal, the positive ions are confined to the near vicinity of their lattice points, whereas the free electrons move freely through the volume of the metal.

Since the electrons have spin half, we treat these electrons as an ideal Fermi gas obeying the Fermi–Dirac statistics. Then, the Fermi energy \( \epsilon_F \) of the electron gas (with \( g = 2 \)) is [see eq. (7.30)]

\[ \epsilon_F = \left( \frac{3\pi^2 N}{V} \right)^{2/3} \left( \frac{\hbar^2}{2m} \right) = (3\pi^2 \rho)^{2/3} \left( \frac{\hbar^2}{2m} \right) \]  \hspace{1cm} (7.50)

In most metals the density is high, and the Fermi temperatures \( T_F \) is of the order of \( 10^4 \text{–} 10^5 \text{ K} \), which is larger than a room temperature \( T = 300^\circ \text{ K} \). This shows that the free electron gas in metals is highly degenerate. Thus

<table>
<thead>
<tr>
<th>Electron density ( \rho (\text{m}^{-3}) )</th>
<th>Momentum ( K_F (\text{m}^{-1}) )</th>
<th>Energy ( \epsilon_F (\text{eV}) )</th>
<th>( T_F (\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ( 4.60 \times 10^{28} )</td>
<td>1.10 \times 10^9</td>
<td>4.7</td>
<td>5.5 \times 10^4</td>
</tr>
<tr>
<td>Na ( 2.50 )</td>
<td>0.90</td>
<td>3.1</td>
<td>3.7</td>
</tr>
<tr>
<td>K ( 1.34 )</td>
<td>0.73</td>
<td>2.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Cu ( 8.50 )</td>
<td>1.35</td>
<td>7.0</td>
<td>8.2</td>
</tr>
<tr>
<td>Ag ( 5.76 )</td>
<td>1.19</td>
<td>5.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Au ( 5.90 )</td>
<td>1.20</td>
<td>5.5</td>
<td>6.4</td>
</tr>
</tbody>
</table>
we can treat the free electron gas as a degenerate ideal Fermi gas. The theory discussed in the preceding section for the degenerate ideal Fermi gas can be applied to the free electrons in a metal.

Let us now discuss the results of the free electron gas. \( \epsilon_F \) in this case is high because the density \( \rho \) is high and the mass of the electron \( m \) is very small.

We first consider the case when \( T \to 0 \), where the total energy of the system is

\[
U_0 = \frac{3}{5} N \epsilon_F
\]

\[= \frac{3N \hbar^2}{10m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} \quad (7.51)
\]

Then, the equation of state of the electron gas at \( T = 0 \) is

\[
P_0 = \frac{2}{5} \frac{N \epsilon_F}{V} \quad (7.52)
\]

This pressure is usually much higher than that of the usual gas, and tends to expand the metal, which is counter balanced by the attractive forces between the atoms within the metal. Thus the free electrons are generally prevented from leaving the metal under this high pressure. However, at very high temperature, some of the electrons may have sufficient energies to escape from the metal.

When the temperature \( T \) is raised from \( T = 0 \), only a very small portion of the electrons is influenced by temperature, the major part of the system remains unaffected. Accordingly, the chemical potential of the free electron gas is given by [see Eq. (7.42)]

\[
\mu = \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \ldots \right] \quad (7.53)
\]

At room temperature \( T \ll T_F \), \( \mu \) is only fractionally below the Fermi energy \( \epsilon_F \). As a good approximation, the chemical potential at \( T \ll T_F \) is equal to the Fermi energy \( \epsilon_F \).

In the low temperature limit when \( T \ll T_F \) the energy of the free electron gas is given by

\[
U = \frac{3}{5} N \epsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T^2}{T_F^2} \right) + \ldots \right] \quad (7.54)
\]

and the specific heat at constant volume is

\[
C_V = \frac{\pi^2}{2} Nk \left( \frac{T}{T_F} \right) + 0 \left( \frac{T}{T_F} \right)^3 \quad (7.55)
\]

From Eq. (7.55), it is clear that when \( T \ll T_F \), the specific heat of the free electron gas in metal is proportional to the absolute temperature \( T \), i.e.

\[
C_V \propto T
\]

This vanishes at absolute zero of temperature.
When we consider the specific heat of metal, it is the sum of the contributions of the free electrons and the lattice vibration. Thus,

$$C_V = (C_V)_{\text{electron}} + (C_V)_{\text{lattice}}$$  \hspace{1cm} (7.56)

where, the first term of (7.56) is the contribution of the free electrons to the specific heat of a metal and given by (7.55), and the second term is the contribution of the lattice vibrations. According to the Debye theory, the contribution of the lattice vibrations to the specific heat of a metal is

$$(C_V)_{\text{lattice}} = 3Nk \left[ 1 - \frac{1}{20} \left( \frac{T_D}{T} \right)^2 + \ldots \right] \quad \text{for} \quad T \gg T_D$$

$$= \frac{12\pi^4}{5} Nk \left( \frac{T}{T_D} \right)^3 \quad \text{for} \quad T \ll T_D$$  \hspace{1cm} (7.57)

where $T_D$ is the Debye temperature of metal, which is around 100 to 400 K. At ordinary temperatures, the specific heat of the free electrons in metal is negligible in comparison to the specific heat of the lattice. At very low temperature, when the Debye $T^3$ law is valid, the contribution of the free electrons is observable. Thus, at low temperatures, the total specific heat of a metal is given by

$$C_V = \frac{\pi^2}{2} Nk \left( \frac{T}{T_F} \right) + \frac{12\pi^4}{5} Nk \left( \frac{T}{T_D} \right)^3$$

$$= \gamma T + \beta T^3$$  \hspace{1cm} (7.58)

where $\gamma$ and $\beta$ are constants characteristic of the metal. The variation of $C_V/T$ against $T^2$ is shown in Fig. 7.6. The results are in good agreement with the experimental values. At sufficiently low temperatures, the linear term predominates, and this allows one to determine the electronic specific heat

![Fig. 7.6 Low temperature specific heat of metal, $C_V/T$ as a function of $T^2$. Experimental values of potassium are shown by circles](image-url)
term from the experiment. The intercept gives the value of $\gamma$, while the value of $\beta$ can be determined from the slope of the curve. However, the theoretical value of $\gamma$ does not agree with experimental values. The ratio of $\gamma_{\text{exp}}$ and $\gamma_{\text{theor}}$ is generally given by the relation

$$\frac{\gamma_{\text{exp}}}{\gamma_{\text{theor}}} = \frac{m^*}{m}$$  \hspace{1cm} (7.59)

where $m^*$ is the thermal effective mass. The value of $\gamma_{\text{exp}}$ is found to be greater than $\gamma_{\text{theor}}$. This difficulty is a consequence of the over-simplifying assumptions made in the free electron model.

### 7.4 RELATIVISTIC DEGENERATE ELECTRON GAS

We now consider the degenerate electron gas when the Fermi momentum of the electron gas is comparable with the characteristic momentum $mc$ of an electron (where $m$ is the rest mass of an electron and $c$ is the velocity of light). In this situation, the dynamics of the electron is relativistic and the energy–momentum relationship for a relativistic particle is

$$\epsilon = \sqrt{c^2p^2 + m^2c^4}$$  \hspace{1cm} (7.60)

instead of non-relativistic relation

$$\epsilon = \frac{p^2}{2m}$$

The number of quantum states in the momentum range $p$ and $p + dp$ is given by

$$g(p) \, dp = \frac{2\pi gV}{\hbar^3} \, p^2 \, dp$$  \hspace{1cm} (7.61)

where $g = 2$ for electron.

The electron gas obeys the Fermi–Dirac statistics. In this case the electrons will be distributed among the various quantum states according to Pauli's exclusion principle. For simplicity, we consider the electron gas in the state of (almost) complete degeneracy. In such a case, all the single particle states up to $\epsilon = \epsilon_F$ are completely filled with one particle per state while all the single particle states with $\epsilon > \epsilon_F$ are empty. Let $P_F$ be the Fermi momentum corresponding to the Fermi energy $\epsilon_F$. They are related by Eq. (7.60) in this case.

The total number of electrons in the gas is given by

$$N = \frac{4\pi gV}{\hbar^3} \int_0^{P_F} p^2 \, dp$$

$$= \frac{4\pi gV}{3\hbar^3} P_F^3$$  \hspace{1cm} (7.62)

so that the Fermi momentum $P_F$ is

$$P_F = \left( \frac{3N}{4\pi gV} \right)^{1/3} \hbar = \left( \frac{3p}{4\pi g} \right)^{1/3} \hbar$$  \hspace{1cm} (7.63)