Chapter 6
Free Electron Fermi Gas

Free electron model:

- The **valence electrons** of the constituent atoms become **conduction electrons** and move about freely through the volume of the metal.
- The **simplest metals are the alkali metals**– lithium, sodium, potassium, *Na*, cesium, and rubidium.
- The **classical theory** had several conspicuous successes, notably, the derivation of the form of Ohm’s law and the relation between the electrical and thermal conductivity.
- The classical theory fails to explain the **heat capacity** and the **magnetic susceptibility** of the conduction electrons. $M = \chi B$
- Why the electrons in a metal can move so freely without much deflections?

(a) A conduction electron is not deflected by ion cores arranged on a periodic lattice, because matter waves propagate freely in a periodic structure.

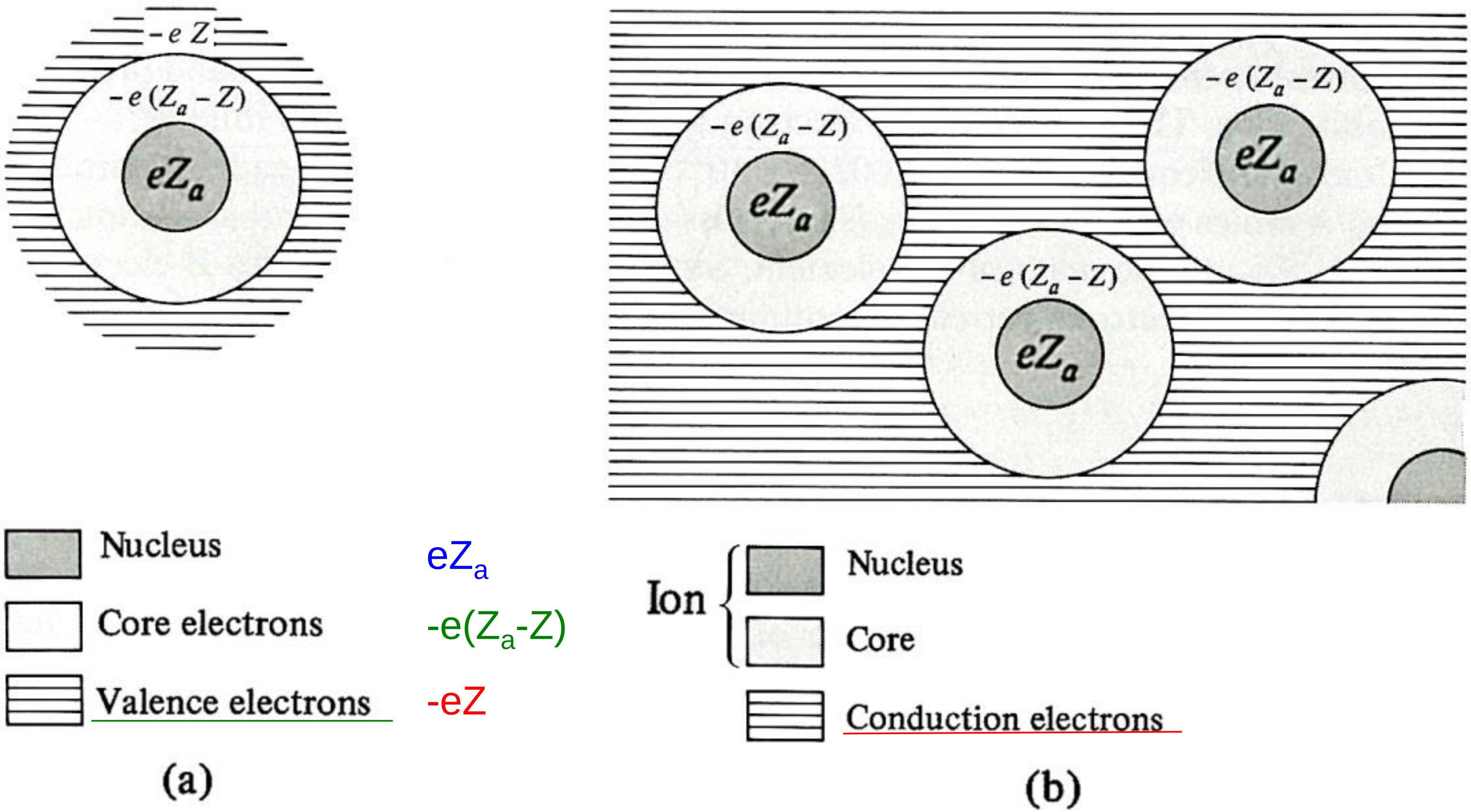
(b) A conduction electron is scattered only infrequently by other conduction electrons.

Pauli exclusion principle.

Free Electron Fermi Gas: a gas of free electrons subject to ***the Pauli Principle***

ELECTRON GAS MODEL IN METALS

Valence electrons form the electron gas



eZ_a

$-e(Z_a-Z)$

$-eZ$

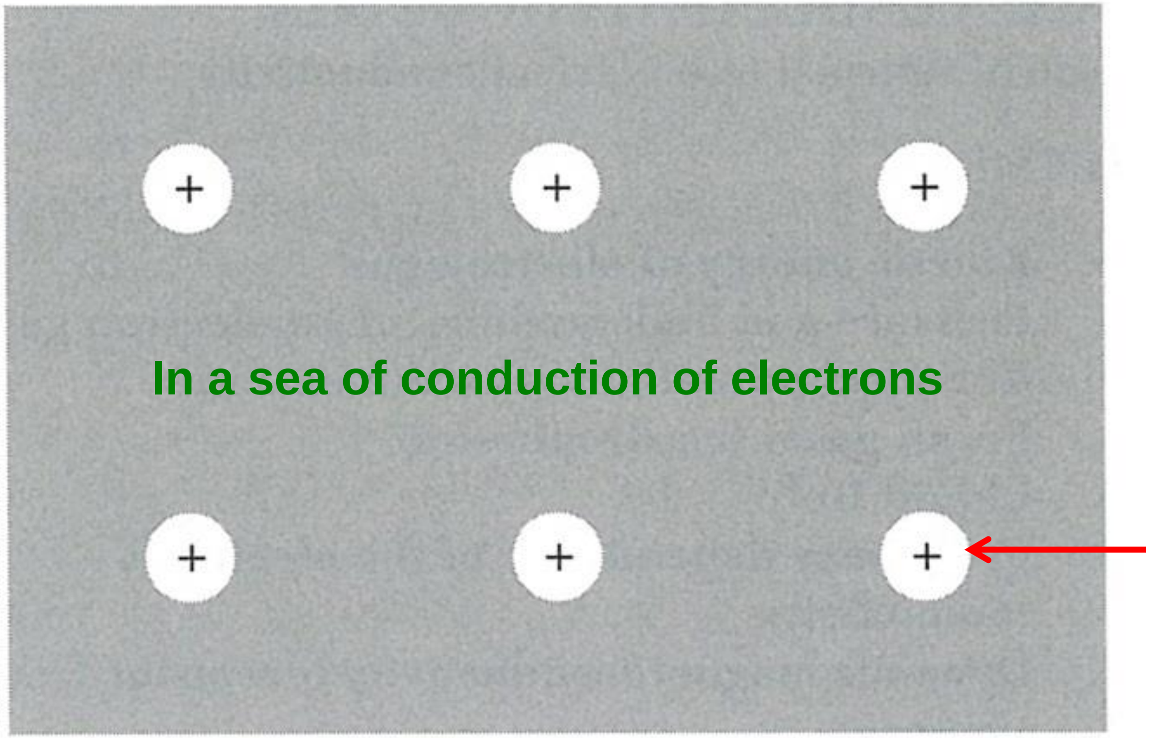
(a)

(b)

Figure 1.1 (a) Schematic picture of an isolated atom (not to scale). (b) In a metal the nucleus and ion core retain their configuration in the free atom, but the valence electrons leave the atom to form the electron gas.

3.66A

0.98A



In a sea of conduction of electrons

Na : simple metal

Core ~ occupy about 15% in total volume of crystal

Figure 1 Schematic model of a crystal of sodium metal. The atomic cores are Na$^+$ ions: they are immersed in a sea of conduction electrons. The conduction electrons are derived from the $3s$ valence electrons of the free atoms. The atomic cores contain 10 electrons in the configuration $1s^2 2s^2 2p^6$. In an alkali metal the atomic cores occupy a relatively small part (~15 percent) of the total volume of the crystal, but in a noble metal (Cu, Ag, Au) the atomic cores are relatively larger and may be in contact with each other. The common crystal structure at room temperature is bcc for the alkali metals and fcc for the noble metals.

Classical Theory (Drude Model)

Drude Model, 1900AD, after Thompson's discovery of electrons in 1897

- Based on the concept of ***kinetic theory*** of neutral ***dilute*** ideal gas

- Apply to the ***dense*** electrons in metals by the free electron gas picture

Classical Statistical Mechanics: Maxwell Boltzmann Distribution

The number of electrons per unit volume with velocity in the range $d\upsilon$ about υ

$$f_B(\upsilon) = n\,(m/\,2\pi k_B T)^{3/2}\ \exp(-m\upsilon^2/2k_B T)$$

Success:

(1) The Ohm's Law

the electrical conductivity

$J = \sigma E\ ,\quad \sigma = n\,e^2\,\tau\,/\,m,$

(2) The Weidmann Frantz Law

$K_e\,/\,(\sigma_e\,T) = L \sim a$ constant

for electrons,

since $K = 1/3\ v_F^{\,2}\ C_v \tau$

Failure:

(1) Heat capacity $C_v \sim 3/2\ NK_B$

The observed heat capacity is only **0.01,** too small.

(2) The observed thermal power Q is also only ~ **0.01, as** $Q = -\,C_v/3ne$

(3) Magnetic susceptibility χ is incorrect.

See Ashroft & Mermin, Ch. 1

$(T_F/T) \longrightarrow$ ***100 times; 0.01 times*** $\longleftarrow (T/T_F)$

We have shown that the **one-dimensional** **energy distribution** is

$$f(v_z) = \sqrt{\frac{m}{2\pi kT}}\, e^{\frac{-mv_z^2}{2kT}}$$

but would like to have a distribution for three dimensions. A basic probability idea is that for three independent events you take the product of the individual probabilities. The three-dimensional probability distribution then takes the form:

$$f(v_x, v_y, v_z) = \left[\frac{m}{2\pi kT}\right]^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)\,/2\,kT}$$

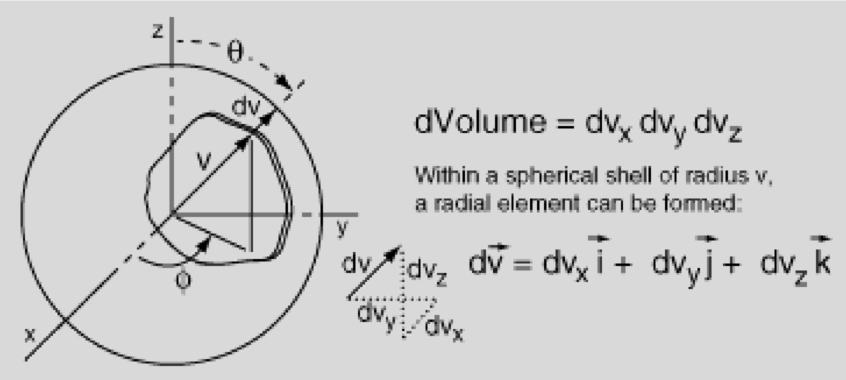
$$= \left[\frac{m}{2\pi kT}\right]^{3/2} e^{-mv^2/2\,kT}$$

$$\text{using} \quad v^2 = v_x^2+v_y^2+v_z^2$$

It must be noted here that **while this has the form of the Boltzmann distribution for kinetic energy**, it does not take into account the fact that there are more ways to achieve a higher velocity. In making the step from this expression to **the Maxwell speed distribution,** this distribution function must be multiplied by the factor ***4πv²*** to account for the density of velocity states available to particles.

Maxwell Speed distribution as a sum over all directions

To put the three-dimensional energy distribution into the form of the Maxwell speed distribution, we need to sum over all directions. One way to visualize that sum is as the development of a spherical shell volume element in "velocity space".

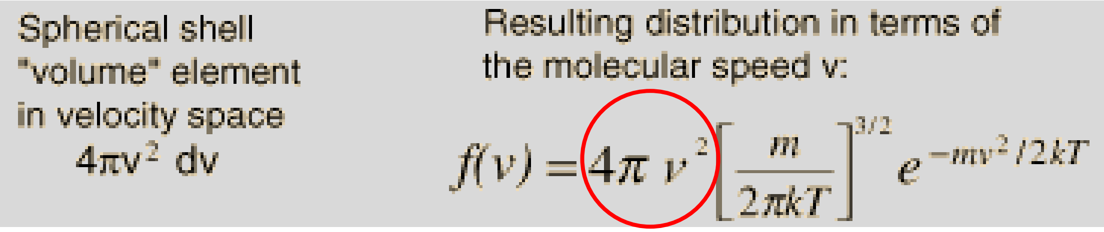


$dVolume = dv_x\, dv_y\, dv_z$

Within a spherical shell of radius v, a radial element can be formed:

$d\vec{v} = dv_x\,\vec{i} + dv_y\,\vec{j} + dv_z\,\vec{k}$

The sum over the angular coordinates is just going to give the area of the sphere, and the radial element dv gives the thickness of the spherical shell. That takes the angular coordinates out of the distribution function and gives a one-parameter distribution function in terms of the "radial" speed element dv.



Spherical shell
"volume" element
in velocity space
$4\pi v^2\, dv$

Resulting distribution in terms of
the molecular speed v:

$$f(v) = 4\pi v^2 \left[\frac{m}{2\pi kT}\right]^{3/2} e^{-mv^2/2kT}$$

Thermal Electrical Effect: (Seeback Effect)

As a temperature gradient is applied to a long thin bar, it should be accompanied by an electrical field directed opposite to the temperature gradient

$$\boxed{\boldsymbol{E} = -\boldsymbol{Q}\,\nabla \boldsymbol{T}}$$

E as the thermal electric field

Q as the thermal power

$$\begin{aligned} Q &= E / \nabla T \\ &= -\,C_v / (3ne) \end{aligned}$$

See Ashcroft & Mermin, Ch. 1, p. 24-25

As in Drude model, C_v and *Q* are 100 times too small !

Drude Model

****** Basic approximations are:***

(1) Between collisions:

-- Neglect electron - ion core interaction --- ***Free electron approximation***
-- Neglect electron - electron interaction --- ***Independent electron approximation***

(2) During collisions:

-- Assuming electrons bouncing off the ion core
-- Assuming some form of scattering

(3) ***Relaxation time approximation****:*

-- Collision mean free time τ
-- Independent of electron position and velocity

(4) The collisions are assumed to maintain **the thermal equilibrium**

Free Electron Gas Model (Sommerfeld) :

***Quantum Statistical Mechanics*:**

*The **Pauli exclusion principle** requires that the replacement of Maxwell Boltzmann distribution with **the Fermi Dirac distribution** as*

$$\boxed{f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}\ .} \qquad (5)$$

*****Can still use the dilute, neutral gas, kinetic picture as in the classical case.***

***** Justifications:***

➢ One can still describe the motion of an electron ***classically*,**
If we can specify its positions and momentum as accurately as possible without violating ***the Heisenberg uncertainty principle.***

➢ One is able to specify the position of an electron on a scale small compared with a distance λ over which the field or temperature varies.

Free Electron Gas Model (Sommerfeld) :

Success:

- Resolve the heat capacity anomaly
- Give correct C_V , thermal power, consistent with the experiments for simple metals
- Good at low *T*, room *T*, but not at medium *T* for noble metals? transition metals?

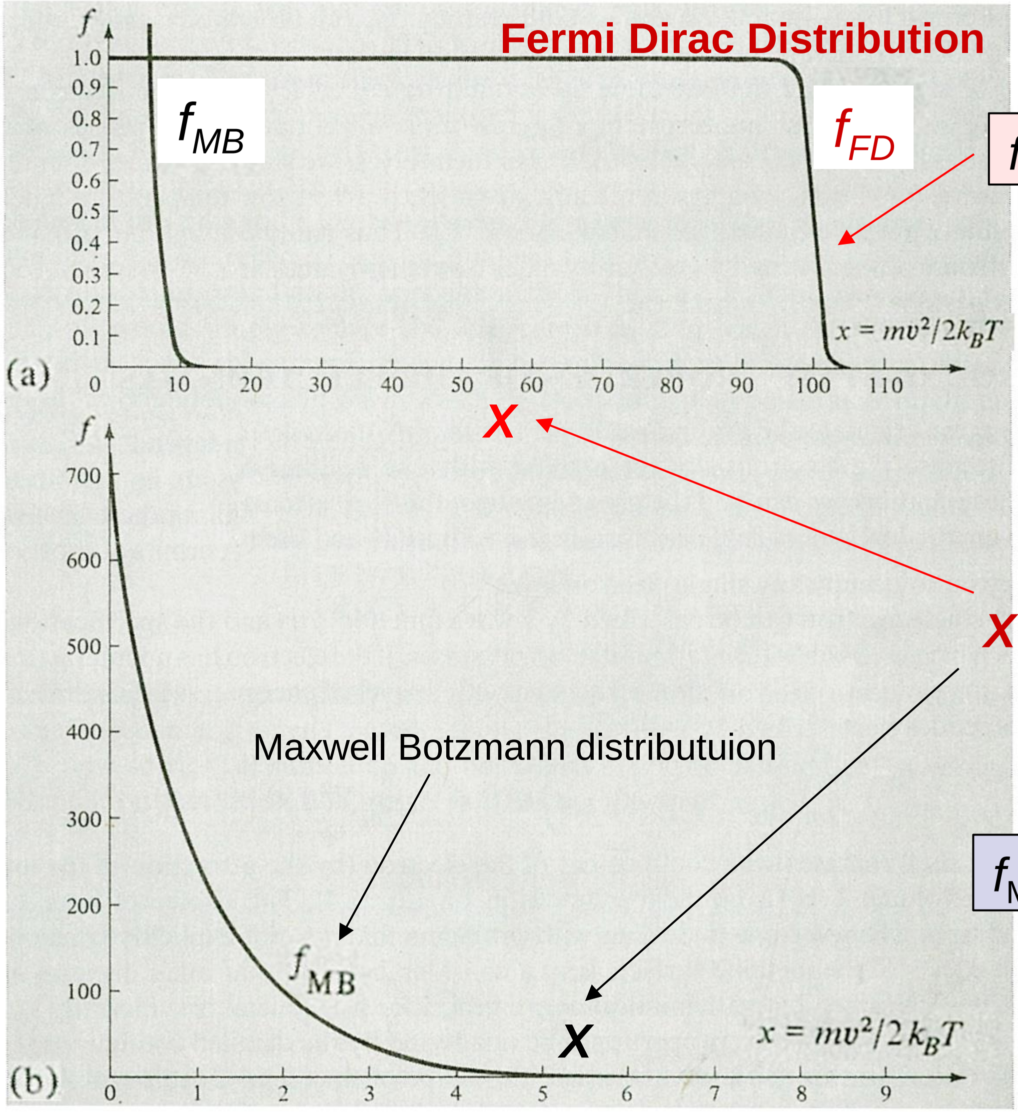
Approximations:

- Neglect the effect of **ions** between collisions.
- The role of **ions** as a source of collision is unspecified.
- The contribution of **ions** to the physical phenomenon is not included.

Ashroft & Mermin: Chapter 2

(a)

(b)



Fermi Dirac Distribution

f_{MB}

f_{FD}

$f_{FD} = [exp(x) + 1]^{-1}$

X

$X = m\upsilon^2/2K_BT$

Maxwell Botzmann distributuion

X

$f_{MB} \propto v^2\, exp(-mv^2/2K_BT)$

Figure 2.1 (a) The Maxwell-Boltzmann and Fermi-Dirac distributions for typical metallic densities at room temperature. (Both curves are for the density given by $T = 0.01T_0$.) The scale is the same for both distributions, and has been normalized so that the Fermi-Dirac distribution approaches 1 at low energies. Below room temperature the differences between the two distributions are even more marked. (b) A view of that part of (a) between $x = 0$ and $x = 10$. The x-axis has been stretched by about a factor of 10, and the f-axis has been compressed by about 500 to get all of the Maxwell-Boltzmann distribution in the figure. On this scale the graph of the Fermi-Dirac distribution is indistinguishable from the x-axis.

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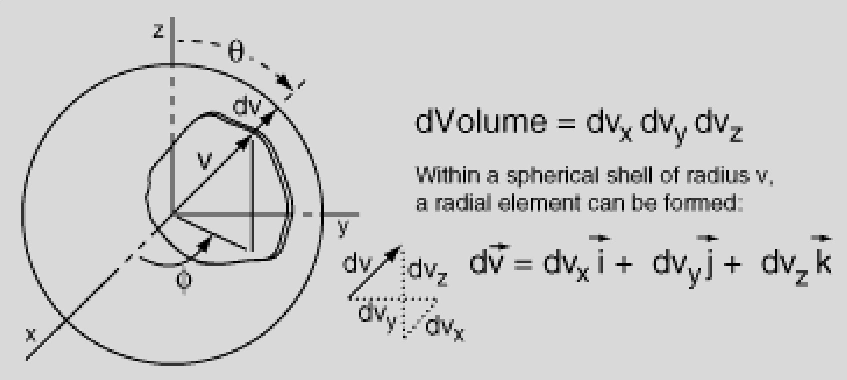

$\mathrm{dVolume} = dv_x\, dv_y\, dv_z$

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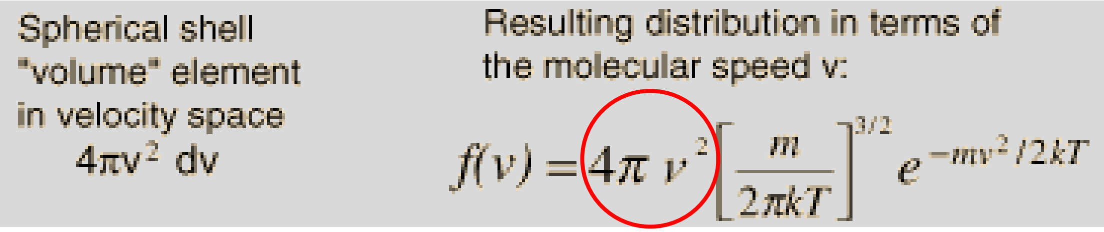


Spherical shell "volume" element in velocity space

$4\pi v^2\, dv$

Resulting distribution in terms of the molecular speed v:

$$f(v) = \boxed{4\pi\, v^2} \left[\frac{m}{2\pi kT}\right]^{3/2} e^{-mv^2/2kT}$$

EFFECT OF TEMPERATURE ON THE FERMI-DIRAC DISTRIBUTION

Ground State : at absolute zero temperature, how about for T > 0 ?

Fermi-Dirac distribution gives the probability that an orbital at energy ϵ will be occupied in an ideal electron gas in thermal equilibrium:

$$\boxed{f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}\ .} \qquad (5)$$

Chemical Potential μ is a function of T, and μ is such that $\int D(\varepsilon) f(\varepsilon)\, d\varepsilon = N$

$\mu = \epsilon$ at $T \longrightarrow 0$

For $\epsilon < \mu$, $f(\epsilon) = 1$; for $\epsilon > \mu$, $f(\epsilon) = 0$

1. At absolute zero $\mu = \epsilon_F$, because in the limit $T \rightarrow 0$ the function $f(\epsilon)$ changes discontinuously from the value 1 (filled) to the value 0 (empty) at $\epsilon = \epsilon_F = \mu$.
2. *At all temperatures $f(\epsilon)$ is equal to $\frac{1}{2}$ when* $\epsilon = \mu$, for then the denominator of (5) has the value 2.
3. The quantity μ is the **chemical potential** (*TP*, Chapter 5), and we see that at absolute zero the chemical potential is equal to the Fermi energy.
4. which $\epsilon - \mu \gg k_B T$; so that $f(\epsilon) \cong \exp[(\mu - \epsilon)/k_B T]$. This limit is called the Boltzmann or Maxwell distribution.

Fermi Dirac Distribution Function

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} \cdot \qquad (5)$$

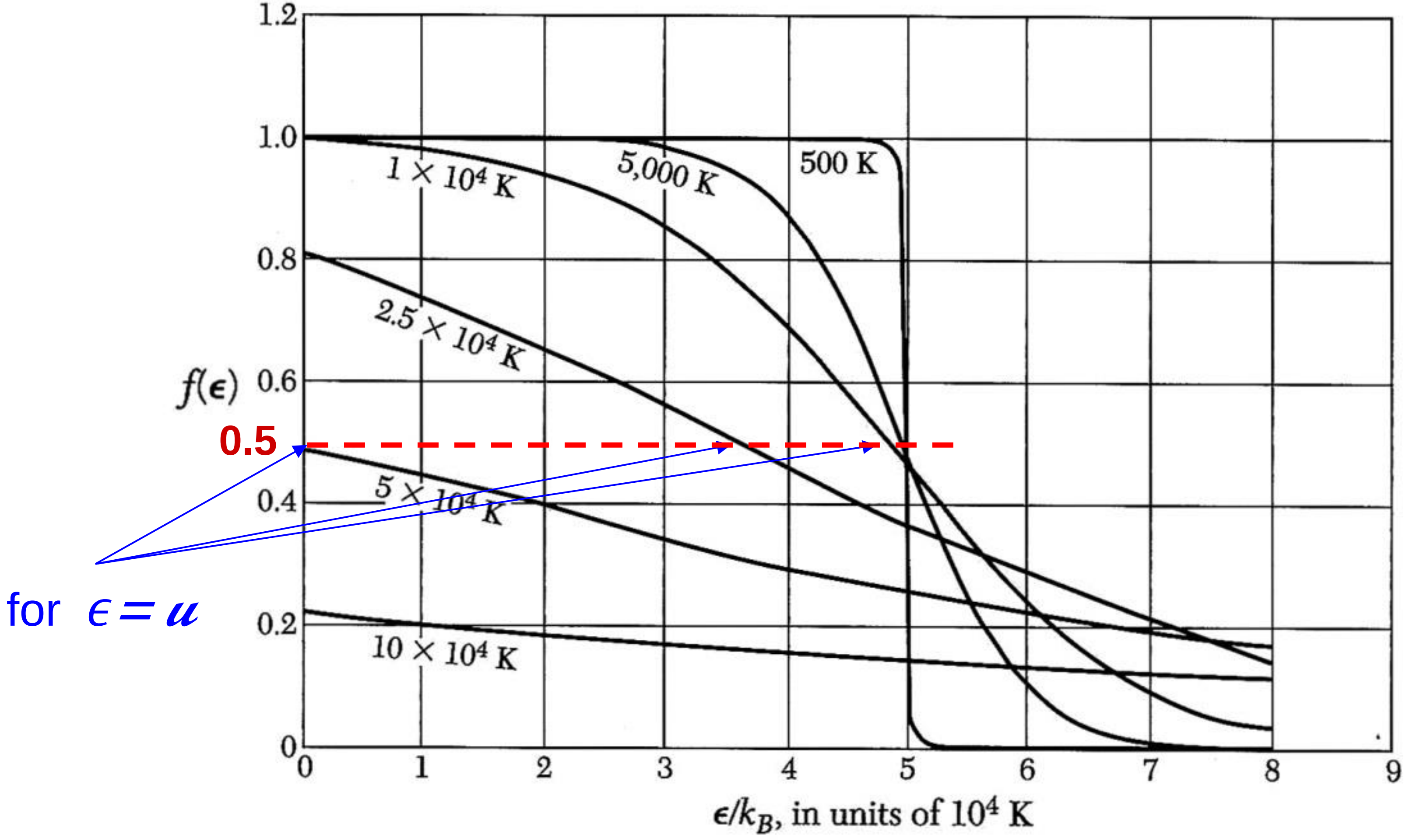


Figure 3 Fermi-Dirac distribution function (5) at the various labelled temperatures, for $T_F \equiv \epsilon_F/k_B = 50{,}000$ K. The results apply to a gas in three dimensions. The total number of particles is constant, independent of temperature. The chemical potential μ at each temperature may be read off the graph as the energy at which $f = 0.5$.

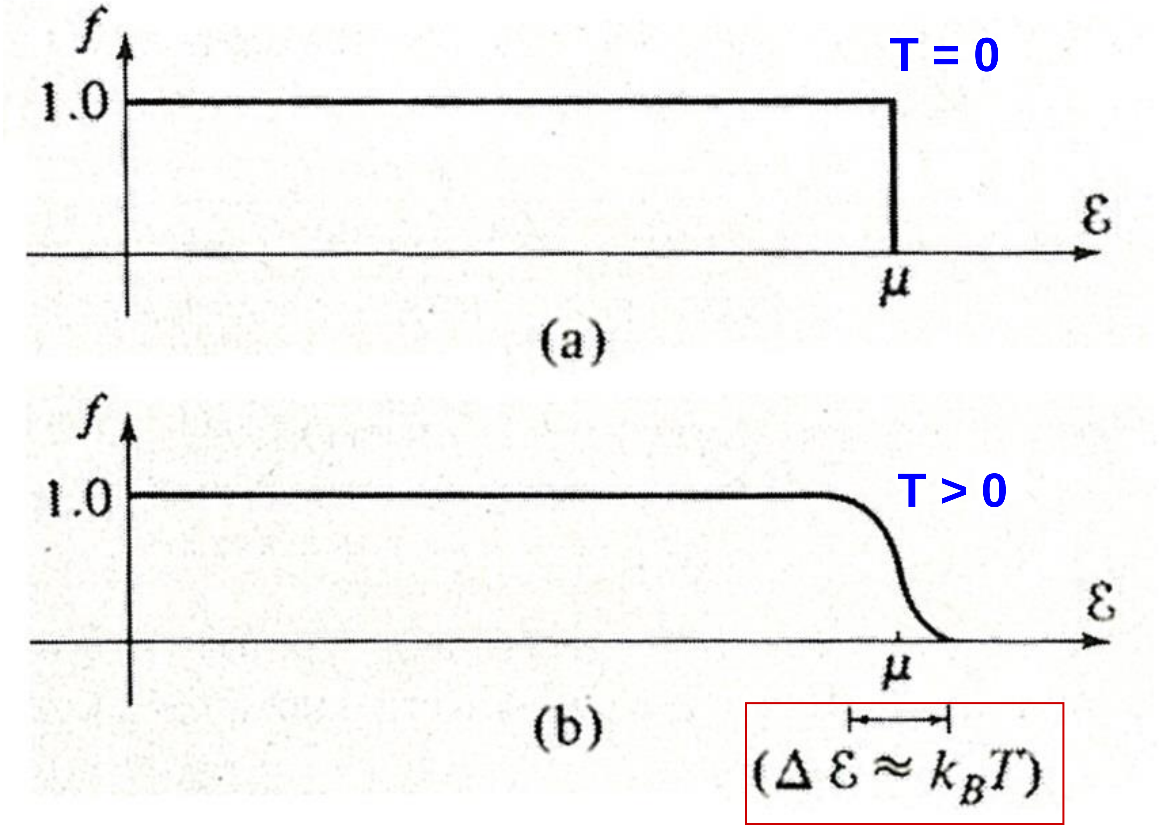


Figure 2.3

The Fermi function, $f(\mathcal{E}) = 1/[e^{\beta(\mathcal{E}-\mu)} + 1]$ versus $\mathcal{E}$ for given μ, at (a) $T = 0$ and (b) $T \approx 0.01\mu$ (of order room temperature, at typical metallic densities). The two curves differ only in a region of order $k_B T$ about μ.

Free Electron Gas in One Dimension

Quantum Theory and Pauli Principle

Electron of mass ***M***, in a *1-D* line of length ***L*** confined to an infinite barrier

The wavefunction $\psi_n(x)$ of the electron is a solution of the Schrödinger equation $\mathcal{H}\psi = \epsilon\psi$; with the neglect of potential energy we have $\mathcal{H} = p^2/2m$, where p is the momentum. In quantum theory p may be represented by the operator $-i\hbar\, d/dx$, so that

$$\mathcal{H}\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n\psi_n \ , \qquad (1)$$

the term **orbital** to denote a solution of the wave equation for a system of only one electron.

The boundary conditions are $\psi_n(0) = 0;\ \psi_n(L) = 0$, as imposed by the infinite potential energy barriers.

Fixed boundary conditions

Standing wave solution

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

$$N\,(\lambda_n/2) = L$$

$$L\left(\frac{2\pi}{\lambda_n}\right) = n\pi$$

$$K = n\pi / L$$

$$\boxed{\psi_n = A\sin\frac{n\pi}{L}x}$$

$$\frac{d\psi_n}{dx} = A\left(\frac{n\pi}{L}\right)\cos\left(\frac{n\pi}{L}x\right) \ ; \quad \frac{d^2\psi_n}{dx^2} = -A\left(\frac{n\pi}{L}\right)^2\sin\left(\frac{n\pi}{L}x\right) \ ,$$

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

the **Pauli exclusion principle**, no two electrons can have all their quantum numbers identical.

In a linear solid the quantum numbers of a conduction electron orbital are n and m_s, where n is any positive integer and the magnetic quantum number $m_s = \pm\frac{1}{2}$, according to spin orientation.

n	m_s	Electron occupancy	n	m_s	Electron occupancy
1	↑	1	3	↑	1
1	↓	1	3	↓	1
2	↑	1	4	↑	0
2	↓	1	4	↓	0

degeneracy.

Let n_F denote the topmost filled energy level,

The condition $2n_F = N$ determines n_F, the value of n for the uppermost filled level.

$n_F = N/2$

Fermi energy ϵ_F

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 .$$

Fermi wavevector k_F

Fermi Temperature T_F

Standing wave solution

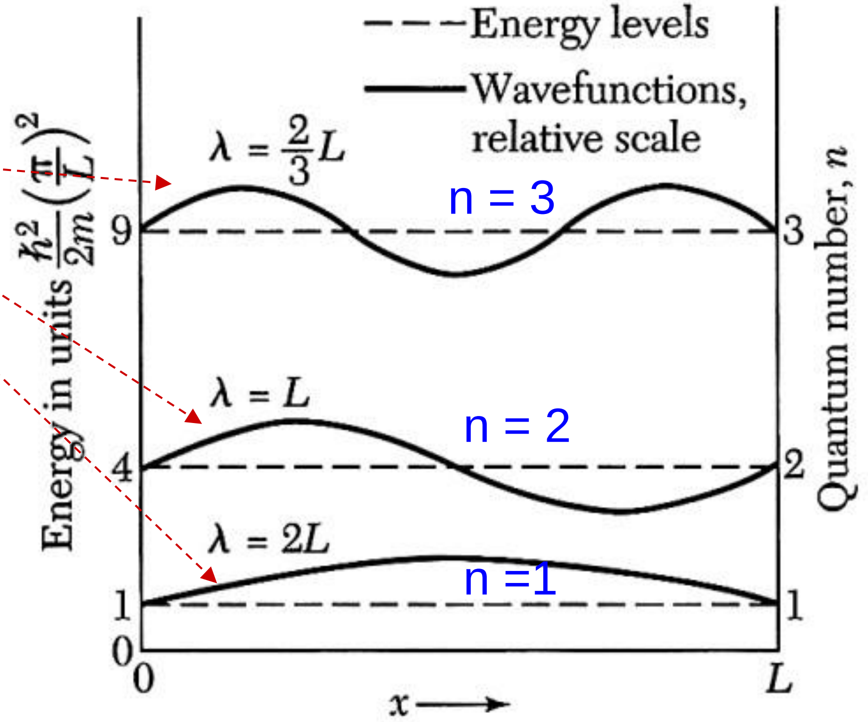
or $N(\lambda_n/2) = L$

$$L\left(\frac{\overset{K}{\overset{\downarrow}{2\pi}}}{\lambda_n}\right) = n\pi$$

$$\boxed{k = n\pi/L}$$

So $\lambda_n = 2L/N$

Figure 2 First three energy levels and wavefunctions of a free electron of mass m confined to a line of length L. The energy levels are labeled according to the quantum number n which gives the number of half-wavelengths in the wavefunction. The wavelengths are indicated on the wavefunctions. The energy ϵ_n of the level of quantum number n is equal to $(h^2/2m)(n/2L)^2$. π^2



FREE ELECTRON GAS IN THREE DIMENSIONS

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}\,\psi_{\mathbf{k}}(\mathbf{r}) \ . \qquad (6)$$

(1) For electrons confined to a cubic of edge ***L*****,** **standing wave solution** $\boxed{k = n\,\pi/L}$

$$\psi_n(\mathbf{r}) = A\sin(\pi n_x x/L)\sin(\pi n_y y/L)\sin(\pi n_z z/L) \ , \qquad (7)$$

(2) Periodic boundary conditions

$$\psi(x+L,y,z) = \psi(x,y,z) \ , \qquad (8)$$

Wave functions satisfying the free particle Schrödinger equation and the periodicity condition are of the form of a traveling plane wave:

$$\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}) \ ,} \longrightarrow \qquad (9)$$

Exp (ikL) = 1

$\boxed{k = \pm n\,2\pi/L}$

$$k_x = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \ \ldots \ , \qquad (10)$$

and similarly for k_y and k_z. Any component of $\mathbf{k}$ of the form $2n\pi/L$

$$\begin{aligned}\exp[ik_x(x+L)] &= \exp[i2n\pi(x+L)/L] \\ &= \exp(i2n\pi x/L)\exp(i2n\pi) = \exp(i2n\pi x/L) = \exp(ik_x x) \ . \qquad (11)\end{aligned}$$

Fermi Sphere
Fermi Surface

At the surface ϵ_f, K_f

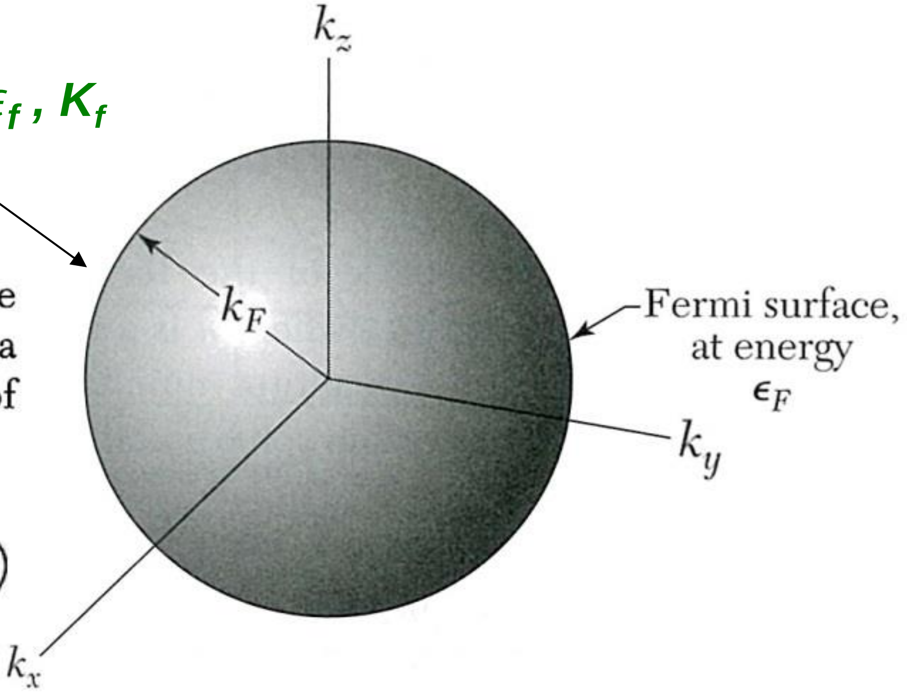


Figure 4 In the ground state of a system of N free electrons the occupied orbitals of the system fill a sphere of radius k_F, where $\epsilon_F = \hbar^2 k_F^2/2m$ is the energy of an electron having a wavevector k_F.

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \ . \qquad (12)$$

the operator $\mathbf{p} = -i\hbar\nabla$, *Linear momentum operator*

$$\underline{\mathbf{p}\psi_{\mathbf{k}}}(\mathrm{r}) = -i\hbar\nabla\psi_{\mathbf{k}}(\mathbf{r}) = \underline{\hbar\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}) \ , \qquad (13)$$

so that the plane wave $\psi_{\mathbf{k}}$ is an eigenfunction of the linear momentum with the eigenvalue $\hbar\mathbf{k}$.

In the ground state of a system of N free electrons, the occupied orbitals may be represented as points inside a sphere in **k** space.

$$\epsilon_F = \frac{\hbar^2}{2m}k_F^2 \ . \qquad (14)$$

at the Fermi surface ϵ_F, k_f

there is one allowed wavevector—that is, one distinct triplet of quantum numbers k_x, k_y, k_z—for the volume element $(2\pi/L)^3$ of **k** space. Thus in the sphere of volume $4\pi k_F^3/3$ the total number of orbitals is

$$2\cdot\frac{4\pi k_F^3/3}{(2\pi/L)^3}=\frac{V}{3\pi^2}k_F^3=N\ , \tag{15}$$

where the factor 2 on the left comes from the two allowed values of m_s, the spin quantum number,

$$k_F=\left(\frac{3\pi^2N}{V}\right)^{1/3}\ , \tag{16}$$

$$\boxed{\epsilon_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2N}{V}\right)^{2/3}\ .} \tag{17}$$

$$v_F=\left(\frac{\hbar k_F}{m}\right)=\left(\frac{\hbar}{m}\right)\left(\frac{3\pi^2N}{V}\right)^{1/3}\ . \tag{18}$$

ϵ_F, V_F, k_F, T_F → See Table 1

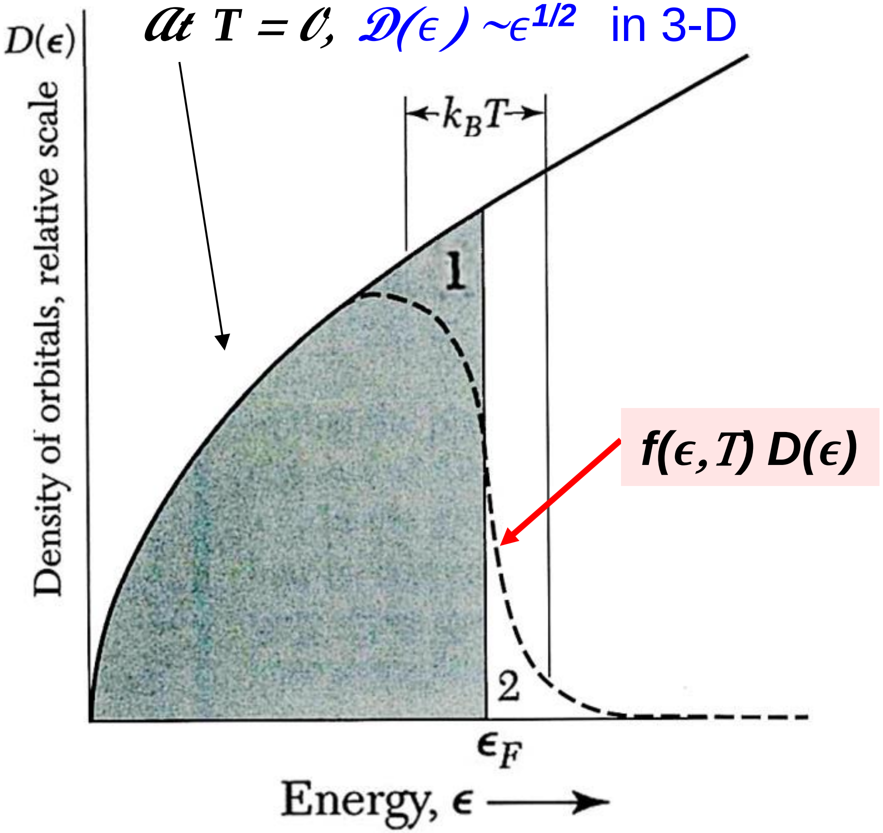
- the number of orbitals per unit energy range, $D(\epsilon)$, called the **density of states.**

From eq. 17
$$N = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2} , \qquad (19)$$

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

$$ln\ N = \frac{3}{2}\ In\ \epsilon\ + constant\ ; \qquad \frac{dN}{N} = \frac{3}{2} \cdot \frac{d\epsilon}{\epsilon}$$

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon} . \qquad (21)$$



At T = 0, $\mathcal{D}(\epsilon) \sim \epsilon^{1/2}$ in 3-D

$f(\epsilon, T)\ D(\epsilon)$

Figure 5 Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density $f(\epsilon, T)D(\epsilon)$ of filled orbitals at a finite temperature, but such that k_BT is small in comparison with ϵ_F. The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to T, for electrons are thermally excited from region 1 to region 2.

Heat Capacity of the Electron Gas

Classical theory, $C_v = 3/2\ NK_B$ ***for electrons***

But the observed electronic contribution at room temperature is usually less than 0.01 of this value.

The question was answered only upon the discovery of the Pauli exclusion principle and the Fermi distribution function.

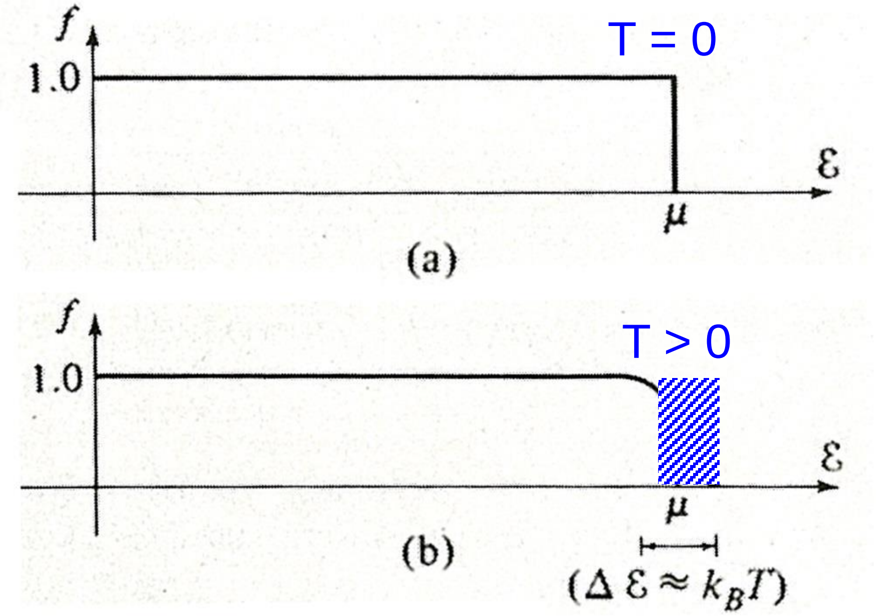


Figure 2.3
The Fermi function, $f(\mathcal{E}) = 1/[e^{\beta(\mathcal{E}-\mu)} + 1]$ versus $\mathcal{E}$ for given μ, at (a) $T = 0$ and (b) $T \approx 0.01\mu$ (of order room temperature, at typical metallic densities). The two curves differ only in a region of order $k_B T$ about μ.

$\Delta N \sim N\ (T/T_F)$, $\Delta U \sim N\ (T/T_F)\ K_B T$

electronic heat capacity $C_{el} = \partial U/\partial T \approx Nk_B(T/T_F)$ X 2 (23)

At room temperature C_{el} is smaller than the classical value $\frac{3}{2}Nk_B$ by a factor of the order of 0.01 or less, for $T_F \sim 5 \times 10^4$ K. → $T/T_F \sim 0.01$

The equipartition theorem

- The name "**equipartition**" means "equal division,"
- The original concept of equipartition was that the total kinetic energy of a system is shared equally among all of its independent parts, *on the average*, once the system has reached thermal equilibrium. Equipartition also makes quantitative predictions for these energies.
- For example, it predicts that every atom of a noble gas, in thermal equilibrium at temperature T, has an average translational kinetic energy of $(3/2)k_B T$, where k_B is the Boltzmann constant. As a consequence, since kinetic energy is equal to 1/2(mass)(velocity)^2, the heavier atoms of xenon have a lower average speed than do the lighter atoms of helium at the same temperature.
- In this example, the key point is that the kinetic energy is quadratic in the velocity.

The equipartition theorem shows that in thermal equilibrium, any degree of freedom (such as a component of the position or velocity of a particle), which appears only quadratically in the energy, has an average energy of $\frac{1}{2} k_B T$ and therefore contributes $\frac{1}{2} k_B$ to the system's heat capacity.

- It follows that the heat capacity of the gas is $(3/2)N k_B$ and hence, in particular, the heat capacity of a mole of such gas particles is $(3/2)N_A k_B$.

If the electrons obeyed classical Maxwell-Boltzmann statistics,

$$F \propto \exp(-\beta\,\epsilon)$$

so that for *all* electrons, then **the equipartition theorem** would give

$$E = 3/2\ N\ K_B T$$

$$C_v = 3/2\ N\ K_B$$

The total energy increase for heating to T from $T = 0$

$$\Delta U \equiv U(T) - U(0) \qquad \Delta U = \int_0^\infty d\epsilon\, \epsilon D(\epsilon) f(\epsilon) - \int_0^{\epsilon_F} d\epsilon\, \epsilon D(\epsilon) \;. \tag{24}$$

We multiply the identity

Since at $T = 0$, $f(\epsilon) = 1$ for $\epsilon < \epsilon_F$

$$N = \int_0^\infty d\epsilon\, D(\epsilon) f(\epsilon) = \int_0^{\epsilon_F} d\epsilon\, D(\epsilon) \tag{25}$$

by ϵ_F to obtain

$$\left(\int_0^{\epsilon_F} + \int_{\epsilon_F}^\infty \right) d\epsilon\, \epsilon_F f(\epsilon) D(\epsilon) = \int_0^{\epsilon_F} d\epsilon\, \epsilon_F D(\epsilon) \;. \tag{26}$$

From (26) to (27), see derivation next page

$$\Delta U = \int_{\epsilon_F}^\infty d\epsilon (\epsilon - \epsilon_F) f(\epsilon) D(\epsilon) + \int_0^{\epsilon_F} d\epsilon (\epsilon_F - \epsilon)[1 - f(\epsilon)] D(\epsilon) \;. \tag{27}$$

The first integral on the right-hand side of (27) gives the energy needed to take electrons from ϵ_F to the orbitals of energy $\epsilon > \epsilon_F$,

The second integral gives the energy needed to bring the electrons to ϵ_F from orbitals below ϵ_F. **$\epsilon < \epsilon_F$**

$$C_{el} = \frac{dU}{dT} = \int_0^\infty d\epsilon (\epsilon - \epsilon_F) \frac{df}{dT} D(\epsilon) \;. \tag{28}$$

Since only ***$f(\epsilon)$*** is temperature dependent

$$\Delta U = \int_0^\infty d\epsilon\ \epsilon D(\epsilon)\, f(\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon D(\epsilon)\ . \tag{24}$$

$$\left(\int_0^{\epsilon_F} + \int_{\epsilon_F}^\infty\right) d\epsilon\ \epsilon_F f(\epsilon) D(\epsilon) = \int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)\ . \tag{26}$$

Eq. (24) May be rewritten as

$$\begin{aligned}\Delta U = &\left(\int_0^{\epsilon_F} + \int_{\epsilon_F}^\infty\right) d\epsilon\ \epsilon D(\epsilon)\, f(\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon\, D(\epsilon) \\ &- \left(\int_0^{\epsilon_F} + \int_{\epsilon_F}^\infty\right) d\epsilon\ \epsilon_F D(\epsilon)\, f(\epsilon) + \int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)\end{aligned}$$

From Eq. (26) there two items are equal.

$$\begin{aligned}= &\int_{\epsilon_F}^\infty d\epsilon\ \epsilon D(\epsilon)\, f(\epsilon) - d\epsilon\ \epsilon_F D(\epsilon)\, f(\epsilon) \\ &+ \int_0^{\epsilon_F} d\epsilon\ \epsilon D(\epsilon)\, f(\epsilon) - d\epsilon\ \epsilon\, D(\epsilon) - d\epsilon\ \epsilon_F D(\epsilon)\, f(\epsilon) + d\epsilon\ \epsilon_F D(\epsilon)\end{aligned}$$

$$= \int_{\epsilon_F}^\infty d\epsilon (\epsilon - \epsilon_F) f(\epsilon) D(\epsilon) + \int_0^{\epsilon_F} d\epsilon (\epsilon_F - \epsilon)[1 - f(\epsilon)] D(\epsilon)\ . \tag{27}$$

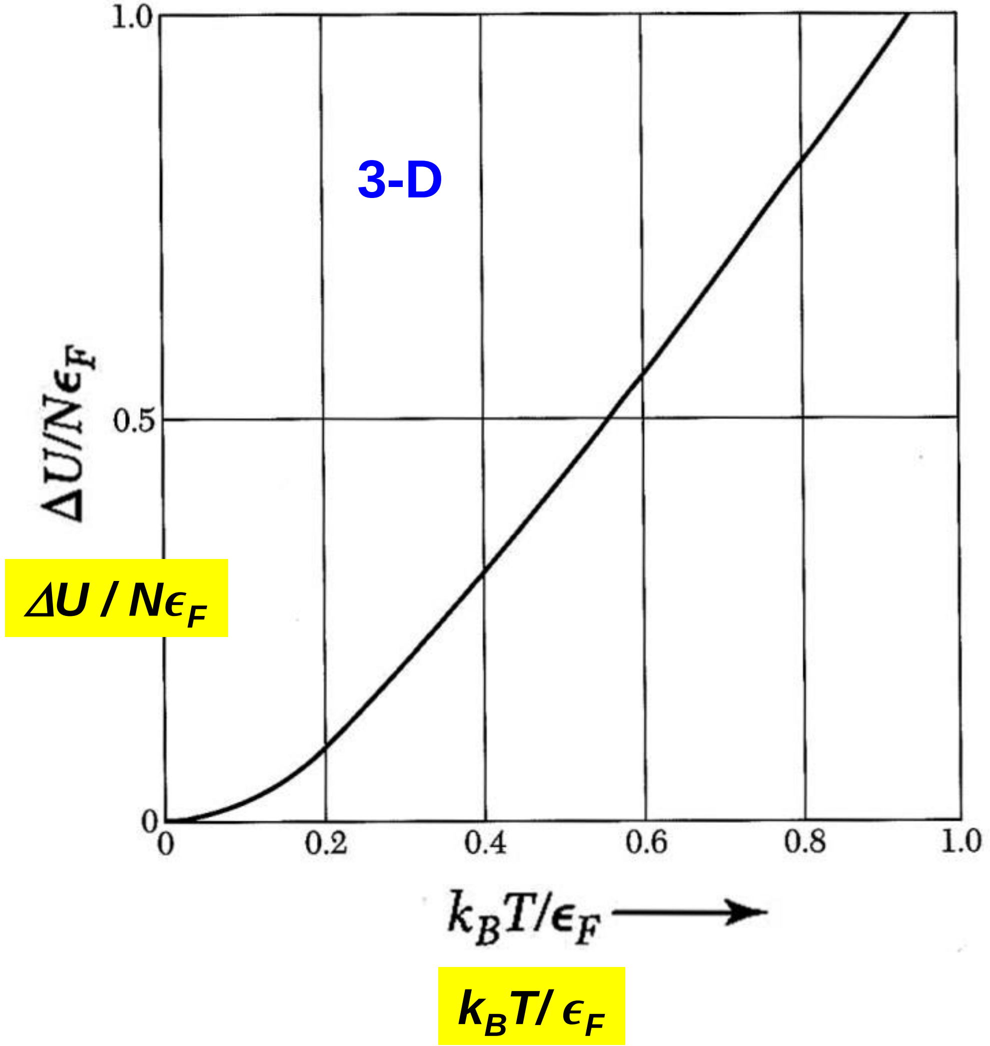


Figure 6 Temperature dependence of the energy of a noninteracting fermion gas in three dimensions. The energy is plotted in normalized form as $\Delta U/N\epsilon_F$, where N is the number of electrons. The temperature is plotted as k_BT/ϵ_F.

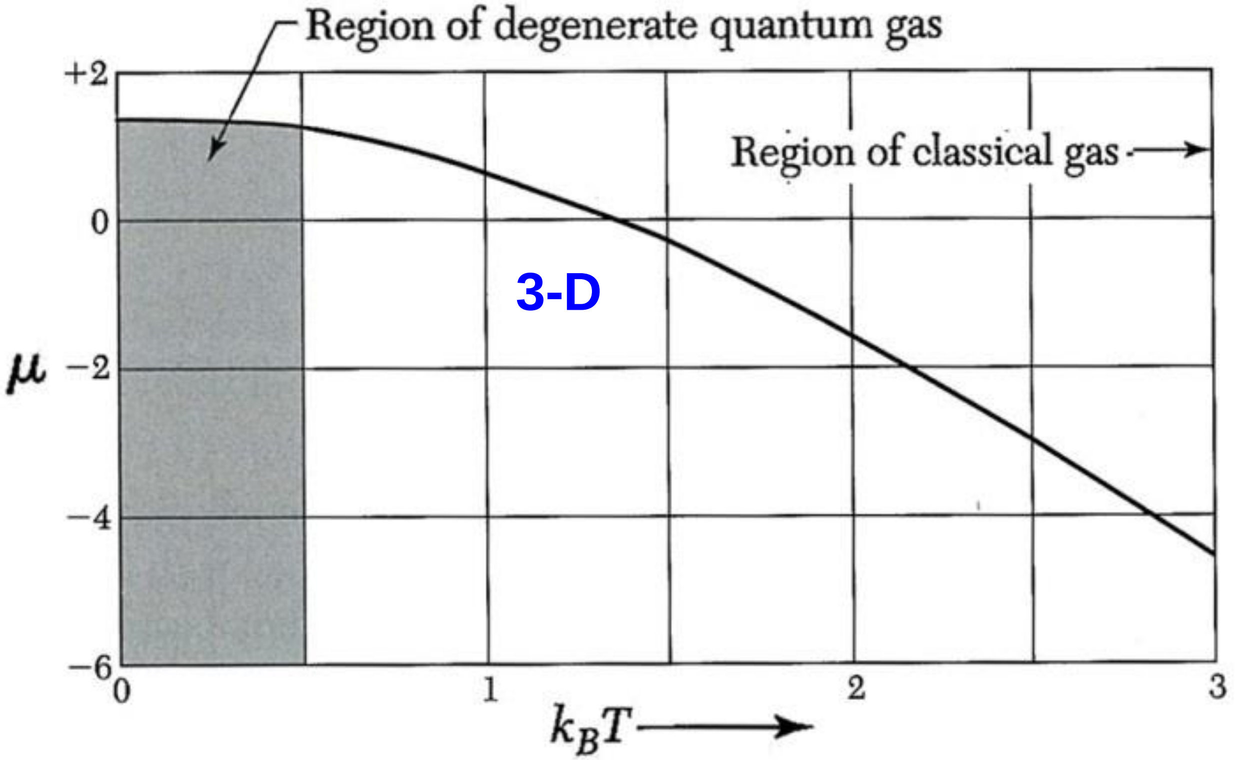
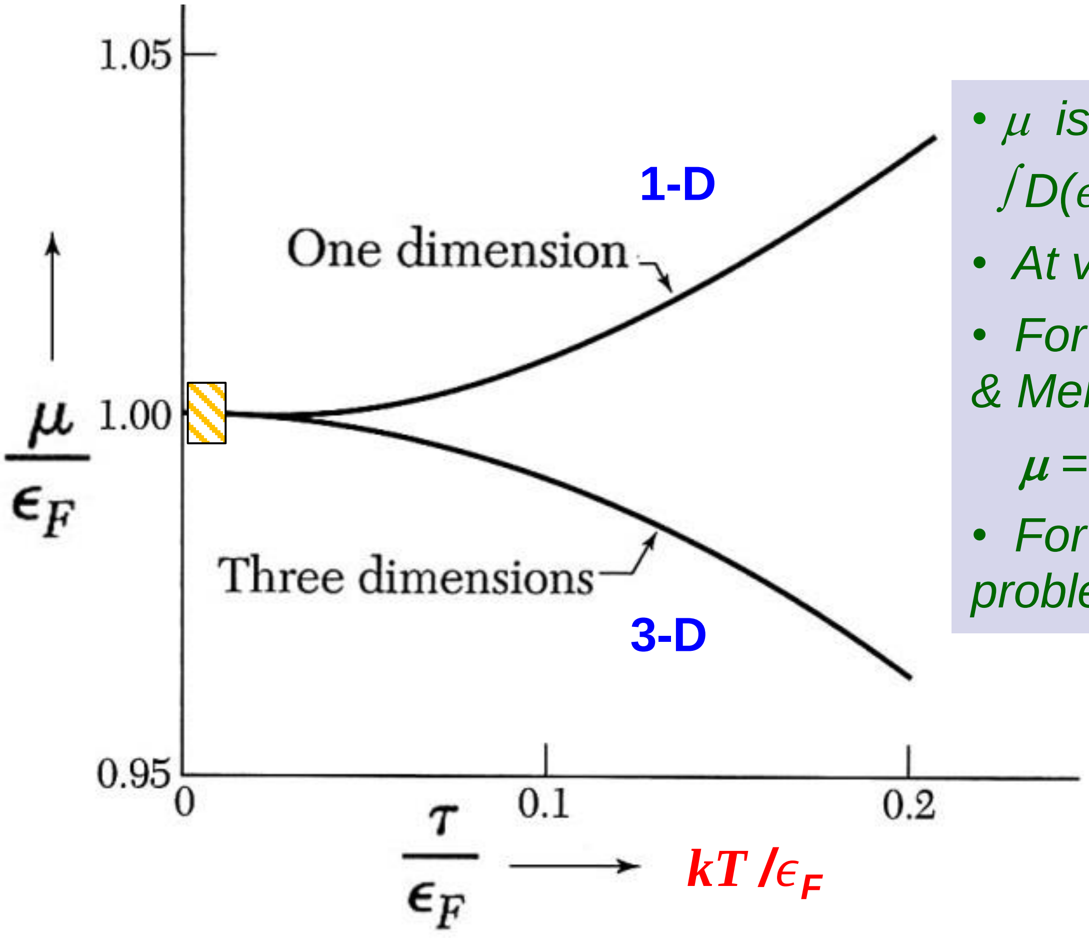


Figure 7 Plot of the chemical potential μ versus temperature as k_BT for a gas of noninteracting fermions in three dimensions. For convenience in plotting, the units of μ and k_BT are $0.763\epsilon_F$.



- *μ is determined by satisfying*
  $\int D(\epsilon)\, f(\epsilon)\, d\epsilon = N$
- *At very low T, $\lim \mu = \epsilon_F$*
- *For the 3-D case, see Ashcroft & Mermin, P. 45-47*
  $$\mu = \epsilon_F \left[1 - 1/3\, (\pi k_B T / 2\epsilon_F)^2 \right]$$
- *For the 2-D case, see Kittel problem 6.3*

Figure 8 Variation with temperature of the chemical potential μ, for free electron Fermi gases in one and three dimensions. In common metals $\tau/\epsilon_F \simeq 0.01$ at room temperature, so that μ is closely equal to ϵ_F. These curves were calculated from series expansions of the integral for the number of particles in the system.

From Fig. 3,

$(\epsilon - \epsilon_F)\, df/dT$ has large positive peaks at energies near ϵ_F. It is a good approximation to evaluate the density of states $D(\epsilon)$ at ϵ_F and take it outside of the integral ; when $k_B T \ll \epsilon_F$ we ignore the temperature dependence of the chemical potential μ in the Fermi-Dirac distribution function and replace μ by the constant ϵ_F. with $\tau \equiv k_B T$,

Judging from Figs. 7 and 8, the variation of μ with T, ***at very low T,*** $\lim \mu = \epsilon_F$

$$\frac{df}{d\tau} = \frac{\epsilon - \epsilon_F}{\tau^2} \cdot \frac{\exp[(\epsilon - \epsilon_F)/\tau]}{\{\exp[(\epsilon - \epsilon_F)/\tau] + 1\}^2} \; . \tag{30}$$

$$\underline{x \equiv (\epsilon - \epsilon_F)/\tau \;\; ,} \tag{31}$$

$$C_{el} = k_B^2 T \boxed{D(\epsilon_F)} \int_{-\epsilon_F/\tau}^{\infty} dx\, x^2 \frac{e^x}{(e^x + 1)^2} \; . \tag{32}$$

We may safely replace the lower limit by $-\infty$ because $\boxed{\epsilon_F/\tau >> 1}$

$$\int_{-\infty}^{\infty} dx\, x^2 \frac{e^x}{(e^x + 1)^2} = \frac{\pi^2}{3} \; , \tag{33}$$

heat capacity of an electron gas is

$$C_{el} = \tfrac{1}{3}\pi^2 D(\epsilon_F) k_B^2 T \ . \tag{34}$$

$$D(\epsilon_F) = 3N/2\epsilon_F = 3N/2k_BT_F \tag{35}$$

$$\boxed{C_{el} = \tfrac{1}{2}\pi^2 N k_B T/T_F \ .} \quad \text{Compare with } C_V = 2Nk_BT/T_F \tag{36}$$

T_F is called the Fermi temperature, where $\epsilon_F = k_BT_F$

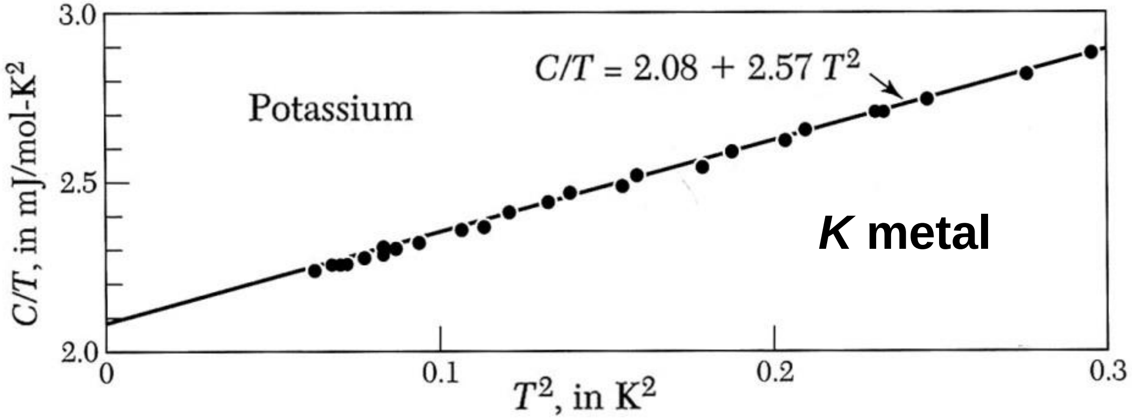


Figure 9 Experimental heat capacity values for potassium, plotted as C/T versus T^2. (After W. H. Lien and N. E. Phillips.)

$\gamma = \frac{1}{2}\pi^2 N k_B T/T_F$ Since $\epsilon_F \propto T_F \propto 1/m$ $\boxed{\therefore \gamma \propto m}$ (See Eq. 17)

At temperatures much below both the Debye temperature θ and the Fermi temperature T_F, the heat capacity of metals may be written as the sum of electron and phonon contributions: $C = \gamma T + AT^3$.

$$\boxed{C/T = \gamma + AT^2 \ ,} \tag{37}$$

γ, called the Sommerfeld parameter. At low T, the electronic term dominates

Express the ratio of the observed to the free electron values of the electronic heat capacity as a ratio of a **thermal effective mass** m_{th} to the electron mass $\boldsymbol{m}$, where $\boldsymbol{m_{th}}$ is defined

$$\boxed{\frac{m_{\text{th}}}{m} \equiv \frac{\gamma(\text{observed})}{\gamma(\text{free})} \ .} \tag{38}$$

See Table 2

The departure from unity involves three separate effects:

A: The interaction of the conduction electrons with the periodic potential of the rigid crystal lattice band effective mass.

B: The interaction of the conduction electrons with phonons.

C: The interaction of the conduction electrons with themselves.

Heavy Fermions.

The heavy fermion compounds include UBe_{13}, $CeAl_3$, and $CeCu_2Si_2$. *f* electrons in these compounds may have inertial masses as high as 1000 m, because of the weak overlap of wavefunctions of *f* electrons on neighboring ions.

(tight binding model)

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

In an electrical field **E** , magnetic field **B**, the force **F** on an electron , the Newton second law of motion becomes

q = -e

(CGS)

$$\boxed{\mathbf{F} = m\frac{d\mathbf{v}}{dt} = \hbar\frac{d\mathbf{k}}{dt} = -e\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right) .} \tag{39}$$

In the absence of collisions the Fermi sphere (Fig. 10) moves in **k** space at a uniform rate by a constant applied electric field.

First considering *B = 0, in zero magnetic field*

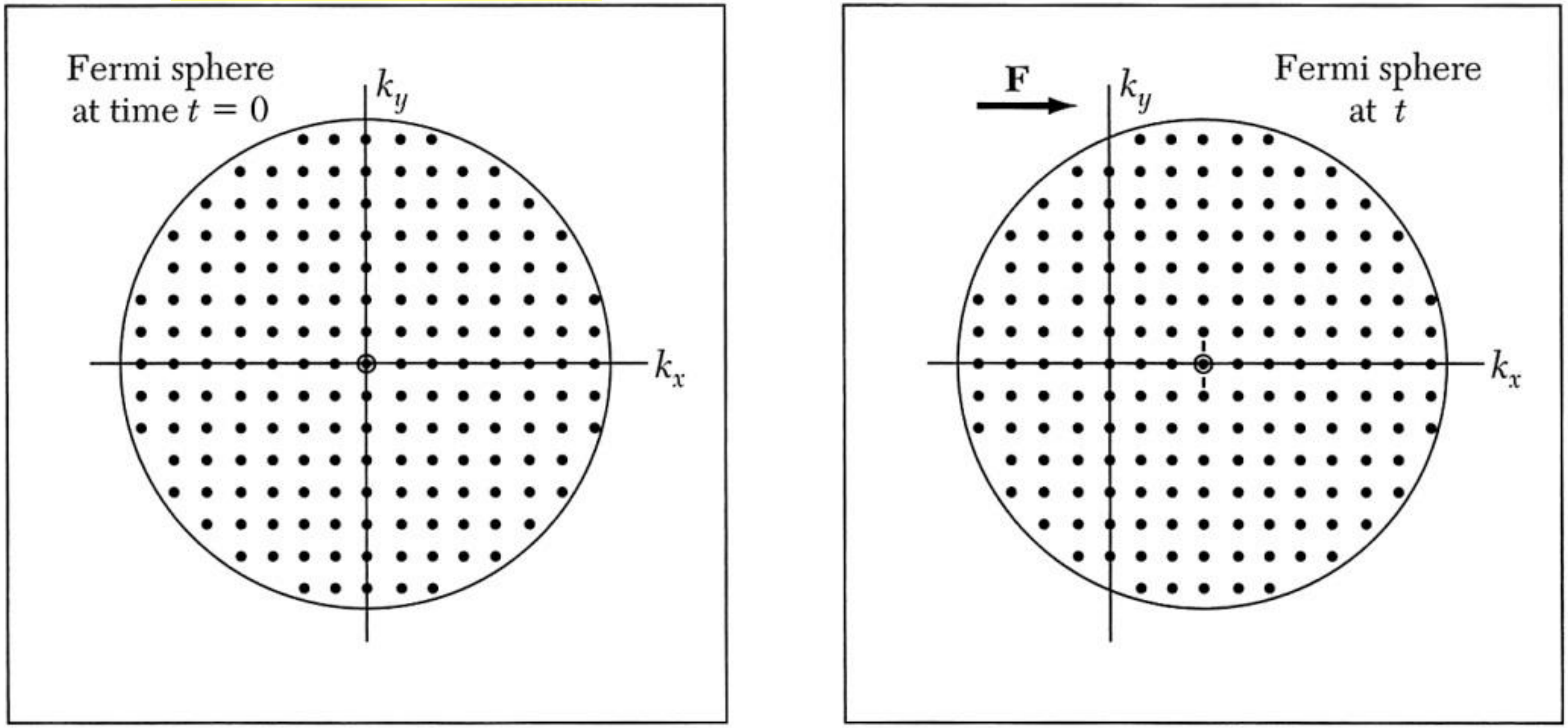
$$\mathbf{k}(t) - \mathbf{k}(0) = -e\mathbf{E}t/\hbar \ . \tag{40}$$

If the field is applied at time *t* then at a later time *t* the sphere will be displaced to a new center at

$$\delta\mathbf{k} = -e\mathbf{E}t/\hbar \ . \tag{41}$$

At the ground state

The displacement of Fermi sphere under force *F*



(a)

(b)

Figure 10 (a) The Fermi sphere encloses the occupied electron orbitals in **k** space in the ground state of the electron gas. The net momentum is zero, because for every orbital **k** there is an occupied orbital at $-\mathbf{k}$. (b) Under the influence of a constant force **F** acting for a time interval t every orbital has its **k** vector increased by $\delta\mathbf{k} = \mathbf{F}t/\hbar$. This is equivalent to a displacement of the whole Fermi sphere by $\delta\mathbf{k}$. The total momentum is $N\hbar\delta\mathbf{k}$, if there are N electrons present. The application of the force increases the energy of the system by $N(\hbar\delta\mathbf{k})^2/2m$.

If the collision time is τ, the displacement of the Fermi sphere in the steady state is given by (41) with $t = \tau$. The incremental velocity is $\mathbf{v} = \hbar\delta\mathbf{k}/m = -e\mathbf{E}\tau/m$.

$q = -e$

$$\mathbf{j} = nq\mathbf{v} = ne^2\tau\mathbf{E}/m \quad . \tag{42}$$

electrical conductivity σ is defined by $\mathbf{j} = \sigma\mathbf{E}$, so that

Conductivity

$$\boxed{\sigma = \frac{ne^2\tau}{m} \quad .} \tag{43}$$

Ohm's Law

electrical resistivity ρ is defined as the reciprocal of the conductivity,

Resistivity

$$\boxed{\rho = m/ne^2\tau \quad .} \tag{44}$$

See Table 3

$\tau \approx 2 \times 10^{-9}$ s at 4 K. The mean free path ℓ of a conduction electron is defined as

$$\underline{\ell = v_F\tau} \quad , \tag{47}$$

v_F is the velocity at the Fermi surface,

we have $v_F = 1.57 \times 10^8$ cm s^{-1} for Cu

$$\ell(4\ \mathrm{K}) \approx 0.3\ \mathrm{cm} \ ; \qquad \ell(3000\ \mathrm{K}) \approx 3 \times 10^{-6}\ \mathrm{cm}.$$

Experimental Electrical Resistivity of Metals

The electrical resistivity of most metals is dominated at room temperature (300 K) by collisions of the conduction electrons with lattice phonons and at liquid helium temperature (4 K) by collisions with impurity atoms and mechanical imperfections in the lattice (Fig. 11).

Lattice phonons

Imperfections

To a good approximation the rates are often independent. And can be summed together

$$\frac{1}{\tau}=\frac{1}{\tau_L}+\frac{1}{\tau_i} \, , \qquad (45)$$

where τ_L and τ_i are the collision times for scattering by phonons and by imperfections, respectively.

The net resistivity is given by

$$\boxed{\rho=\rho_L+\rho_i \quad ,} \qquad (46)$$

Since $\rho \sim 1/\tau$

Often ρ_L is independent of the number of defects when their concentration is small, and often ρ_i is independent of temperature.

This empirical observation expresses ***Matthiessen's Rule.***

The residual resistivity, $\rho_i(0)$, is the extrapolated resistivity at 0 K because ρ_L vanishes as $T \rightarrow 0$. The lattice resistivity, $\rho_L(T) = \rho - \rho_i(0)$, is the same for different specimens of a metal, even though $\rho_i(0)$ may itself vary widely.

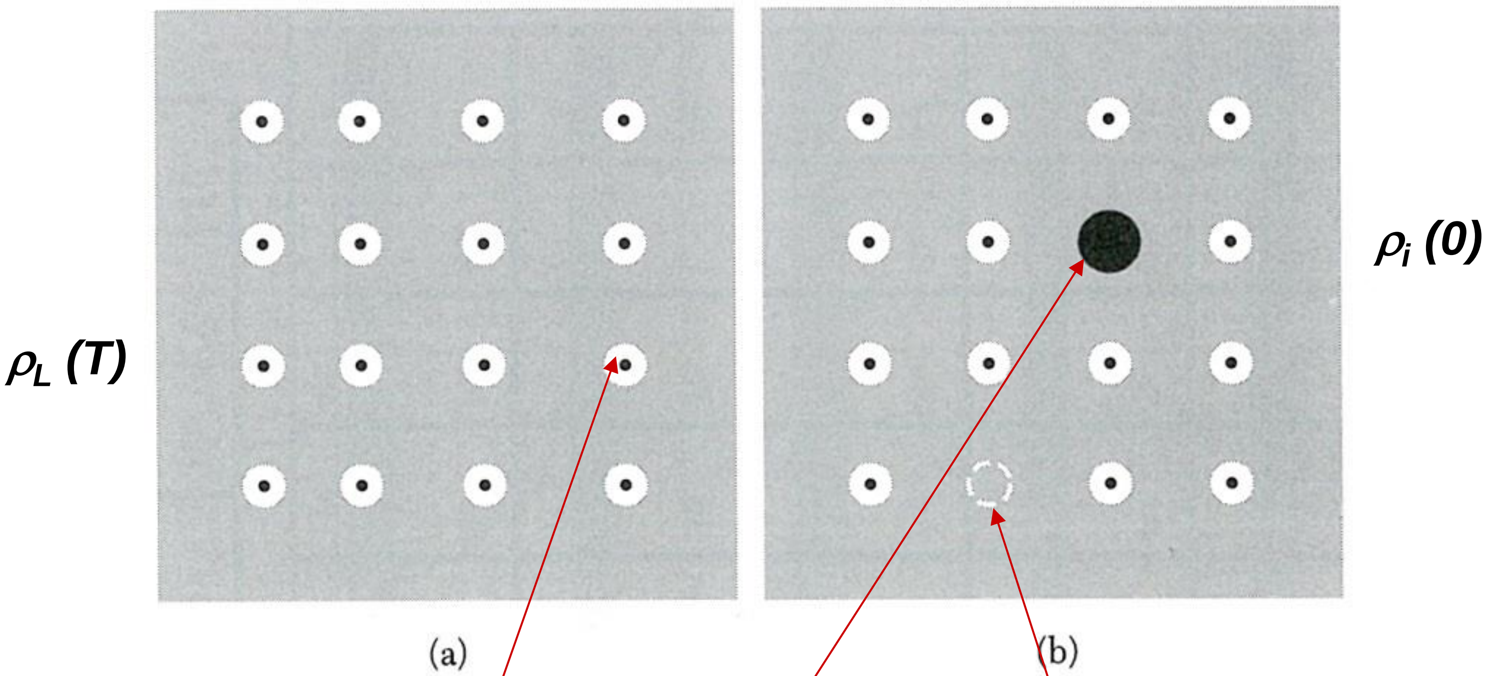
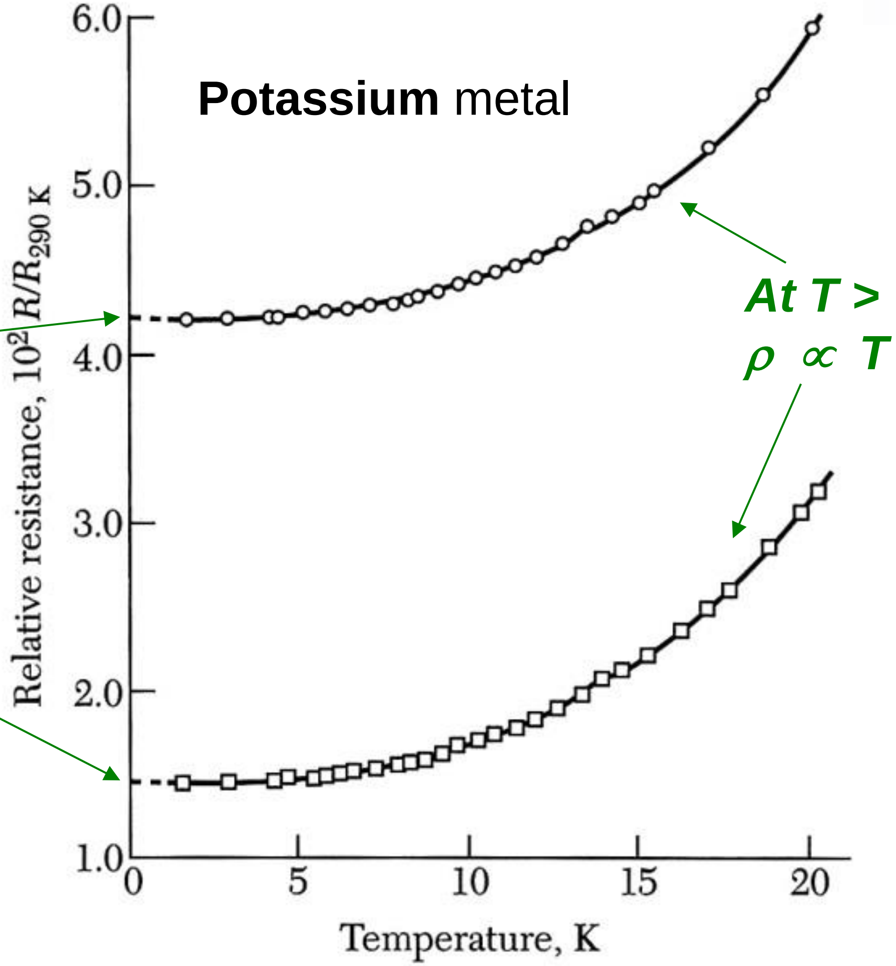


Figure 11 Electrical resistivity in most metals arises from collisions of electrons with irregularities in the lattice, as in (a) by phonons and in (b) by impurities and vacant lattice sites.

Resistivity Ratio = ρ (300K)/ ρ_i(0)

resistivity ratio of a specimen is usually defined as the ratio of its resistivity at room temperature to its residual resistivity. It is a convenient approximate indicator of sample purity.



At $T > \theta$
$\rho \propto T$

Different $\rho_i(0)$, but the same ρ_L

Figure 12 Resistance of potassium below 20 K, as measured on two specimens by D. MacDonald and K. Mendelssohn. The different intercepts at 0 K are attributed to different concentrations of impurities and static imperfections in the two specimens.

The temperature-dependent part of the electrical resistivity is proportional to the rate at which an electron collides with thermal phonons.

One simple limit is at temperatures over the Debye temperature θ: here the phonon concentration is proportional to the temperature T, so that $\rho \propto T$ for $T > \theta$.

$N_{ph} \propto T$ $\rho \propto T$

Umklapp Scattering

Umklapp scattering of electrons by phonons (Chapter 5) accounts for most of the electrical resistivity of metals at low temperatures. These are electron-phonon scattering processes in which a reciprocal lattice vector ***G*** is involved, the normal electron-phonon collision **k'** = **k** + **q**.

Normal process

This scattering is an umklapp process, **k' = k + q + G**

Umklapp process

q_o: the minimum phonon wavevector for Umklapp process

At low enough temperatures the number of phonons available for umklapp scattering falls as $exp\,(-\theta_U/T)$,

where q_o, θ_u are related to the geometry of the Fermi surface

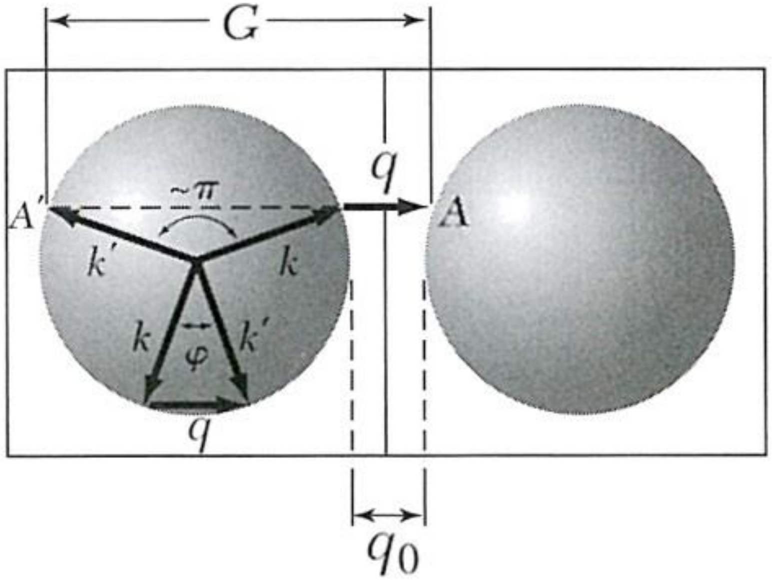


Figure 13 Two Fermi spheres in adjacent zones: a construction to show the role of phonon umklapp processes in electrical resistivity.

Bloch obtained an analytic result for the dominating "normal scattering", with $\rho_L \propto T^5/\theta^6$ at very low temperatures.

Bloch's T^5 Law

The temperature dependence of resistivity:

The electrical resistivity of most materials changes with temperature.

If the temperature *T* does not vary too much, a linear approximation is typically used:

$$\rho(T) = \rho_0[1 + \alpha(T - T_0)]$$

Metals

In general, electrical resistivity of metals increases with temperature. Electron–phonon interactions can play a key role. At high temperatures, the resistance of a metal increases linearly with temperature. As the temperature of a metal is reduced, the temperature dependence of resistivity follows a power law function of temperature.

Mathematically the temperature dependence of the resistivity ρ of a metal is given by the Bloch–Grüneisen formula:

$$\rho(T) = \rho(0) + A\left(\frac{T}{\Theta_R}\right)^n \int_0^{\frac{\Theta_R}{T}} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx$$

A is a constant that depends on the velocity of electrons at the Fermi surface, the Debye radius and the number density of electrons in the metal. **θ_R** is the Debye temperature as obtained from resistivity measurements and matches very closely with the values of Debye temperature obtained from specific heat measurements.

n is an integer that depends upon the nature of interaction.

1. **n=5** implies that the resistance is due to scattering of **electrons by phonons**, (simple metals).
2. **n=3** implies that the resistance is due to **s-d** electron scattering, (as is the case for transition metals).
3. **n=2** implies that the resistance is due to **electron–electron** interaction.

MOTION IN MAGNETIC FIELDS

The free particle acceleration term is $(\hbar d/dt)\,\delta\mathrm{k}$ and the effect of collisions (the friction) is represented by $\hbar\delta\mathrm{k}/\tau$, where τ is the collision time. The equation of motion is

$$\mathbf{F} = -e\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right)\;; \qquad (49)$$

$$\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)\delta\mathbf{k} = \mathbf{F}\ . \qquad (48)$$

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v}\times\mathbf{B})$$

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)\mathbf{v} = -e\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right)\ . \qquad (50)$$

B is along the z axis

(CGS)

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)v_x = -e\left(E_x + \frac{B}{c}v_y\right)\;;$$

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)v_y = -e\left(E_y - \frac{B}{c}v_x\right)\;; \qquad (51)$$

$$m\left(\frac{d}{dt}+\frac{1}{\tau}\right)v_z = -eE_z\ .$$

In a steady state in a static electric field the time derivatives are zero,

$$v_x = -\frac{e\tau}{m}E_x - \omega_c\tau v_y\;; \qquad v_y = -\frac{e\tau}{m}E_y + \omega_c\tau v_x\;; \qquad v_z = -\frac{e\tau}{m}E_z\ , \qquad (52)$$

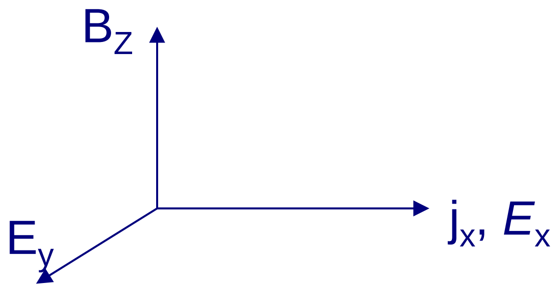
$\omega_c = eB/mc$ is the **cyclotron frequency.**

Hall Effect

The Hall field is the electric field developed across two faces of a conductor, in the direction of ***j* x *B*.**

If current cannot flow out of the rod in the *y* direction we must have $\delta V_y = 0$ and $V_y = 0$, transverse electric field $E_y = -\omega_c \tau E_x = -\frac{eB\tau}{mc} E_x$; (53)

(SI) $$E_y = -\omega_c \tau E_x = -\frac{eB\tau}{m} E_x \ .$$



Hall coefficient. $$\boxed{R_H = \frac{E_y}{j_x B}}$$

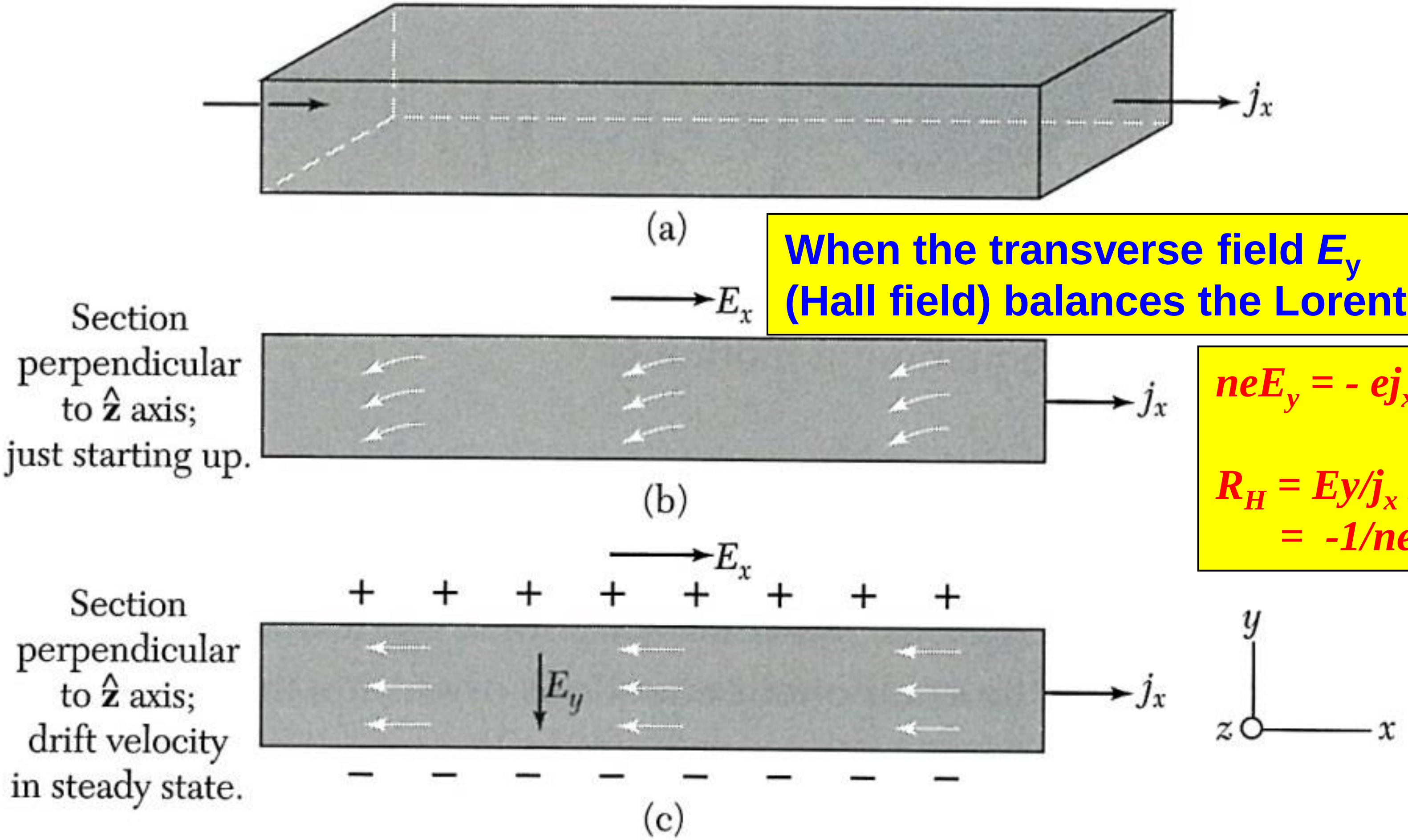
Hall resistance

(CGS) $$R_H = -\frac{eB\tau E_x/mc}{ne^2\tau E_x B/m} = -\frac{1}{nec} \ ; \qquad (55)$$

(SI) $$\boxed{R_H = -\frac{1}{ne} \ .}$$

assume all relaxation τ for both thermal and electrical conduction are equal.

$$\boldsymbol{\rho_H = BR_H = E_y / j_x} \qquad (55a)$$



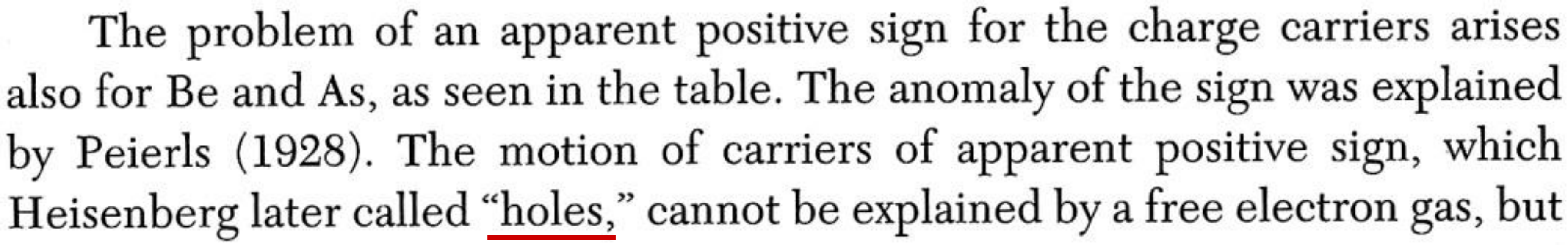
When the transverse field E_y (Hall field) balances the Lorentz force

$$neE_y = -ej_xB/c$$

$$R_H = Ey/j_x B$$
$$= -1/nec$$

Figure 14 The standard geometry for the Hall effect: a rod-shaped specimen of rectangular cross-section is placed in a magnetic field B_z, as in (a). An electric field E_x applied across the end electrodes causes an electric current density j_x to flow down the rod. The drift velocity of the negatively-charged electrons immediately after the electric field is applied as shown in (b). The deflection in the $-y$ direction is caused by the magnetic field. Electrons accumulate on one face of the rod and a positive ion excess is established on the opposite face until, as in (c), the transverse electric field (Hall field) just cancels the Lorentz force due to the magnetic field.

See R_H listed in Table 4



The problem of an apparent positive sign for the charge carriers arises also for Be and As, as seen in the table. The anomaly of the sign was explained by Peierls (1928). The motion of carriers of apparent positive sign, which Heisenberg later called "holes," cannot be explained by a free electron gas, but by the energy band theory.

Al, In are in disagreements with the prediction, with 1 positive hole, not 3 negative electrons

Thermal conductivity of Metals

From eq. (36) for **C_V** in **K, *and*** **$\epsilon_F = 1/2\ mv_F^2$**

$C_V = 1/2\pi^2 Nk_BT/T_F$

$$K_{el} = \frac{\pi^2}{3}\cdot\frac{nk_B^2T}{mv_F^2}\cdot v_F\cdot\ell = \frac{\pi^2nk_B^2T\tau}{3m} \ . \qquad (56)$$

$$\frac{K}{\sigma} = \frac{\pi^2k_B^2Tn\tau/3m}{ne\tau^2/m} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2T \ . \qquad (57)$$

See Table 5 for *L*

The **Lorenz number** L is defined as $L = K/\sigma T$, (58)

Ratio of Thermal to Electrical Conductivity

The **Wiedemann-Franz law** states that for metals at not too low temperatures the ratio of the thermal conductivity to the electrical conductivity is directly proportional to the temperature, with the value of the constant of proportionality independent of the particular metal.

$$\boxed{L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2} = 2.72\times10^{-13}\ (\text{erg/esu-deg})^2$$
$$= 2.45\times10^{-8}\ \text{watt-ohm/deg}^2 \ . \qquad (59)$$

This remarkable result involves neither n nor m. It does not involve τ, if the relaxation times are identical for electrical and thermal processes.

Home work, Chapter 6

- No.1
- No.3
- No.6