Elements
of Solid State Physics

Electron Gas and Metals

Agenda

1. Introduction – Classical Gas vs. Quantum Gas

2. Metals and the Electron Gas Model

3. Properties of the Electron Gas

4. Summary

Classical Gas vs. Quantum Gas

Introduction

Recall that the distribution function, defining the probability $f_B(E)dE$ of finding the system that is in equilibrium with a large reservoir in a state with energy from (E, E + dE), is

$$f_B(E) = \frac{1}{Z} \exp\left(-\frac{E}{k_B T}\right)$$

This distribution function describes very well systems of classical particles (or distinguishable, i.e. non-identical quantum particles).

However, if we want to discuss systems of identical, that is indistinguishable quantum particles, we need to take into account the fact whether these particles are bosons or fermions.

Bosons and Fermions

Recall that quantum particles in 3D are either *bosons* (s = 0, 1, 2,...) or *fermions* (s = 1/2, 3/2, 5/2,...).

The corresponding distribution functions are:
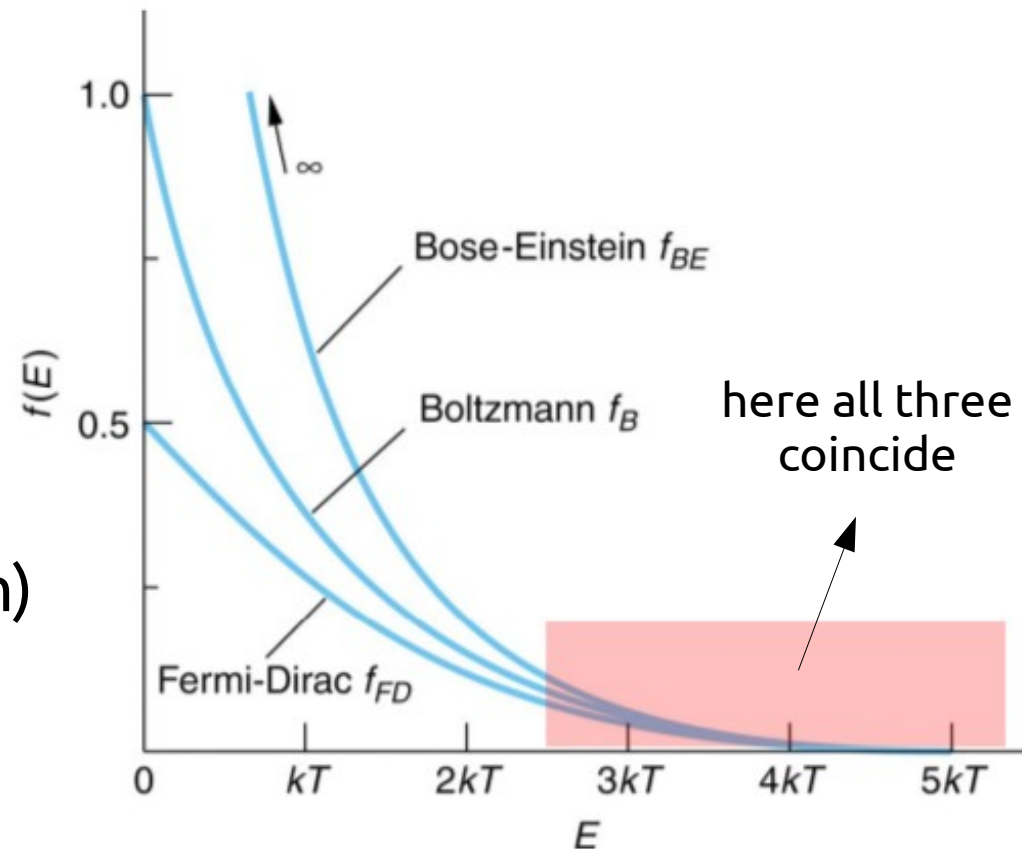
Fermions
(Fermi-Dirac distribution function)

$$f_{\mathrm{FD}}(E) = \frac{1}{Ae^{E/k_BT} + 1}$$

💬

Bosons
(Bose-Einstein distribution function)

$$f_{\mathrm{BE}}(E) = \frac{1}{Ae^{E/k_BT} - 1}$$

[in this graph A=1]

Comment. (In)distinguishability Criterion

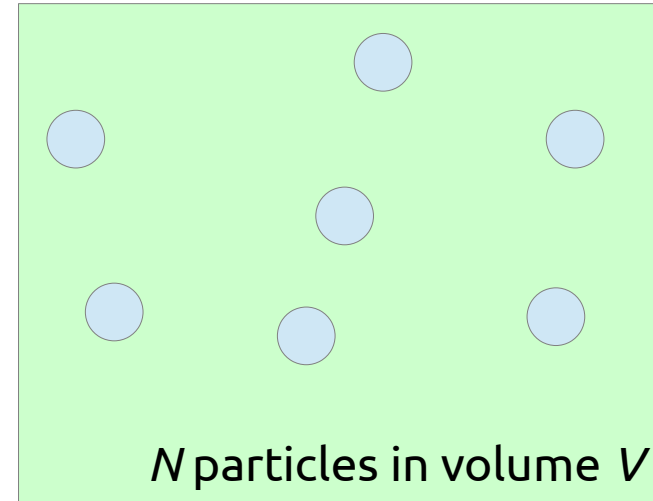Two Identical particles A and B are distinguishable if

💬

de Broglie wavelengths of the particles are much shorter that the separation between them.

[It means that there is no interference effects between particles' de Broglie waves.]

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2m\left(\frac{3}{2}k_BT\right)}} = \frac{h}{\sqrt{3mk_BT}} \ll \left(\frac{V}{N}\right)^{1/3}$$

N particles in volume V

$$\boxed{\frac{h}{\sqrt{3mk_BT}}\left(\frac{N}{V}\right)^{1/3} \ll 1}$$

Conclusion: identical particles are distinguishable if the temperature is high and the density (concentration) of particles is low.

Examples

(a) ^{4}He atoms have spin 0 (hence are bosons) and make up 5.26 x 10^{-6} of the molecules in the atmosphere. Can the Boltzmann distribution be used to predict the thermal properties of atmospheric Helium at 273 K?

$$\frac{N}{V} = \frac{6.022 \times 10^{23} \times 5.26 \times 10^{-6}}{2.24 \times 10^{-2} \text{ m}^3} = 1.41 \times 10^{20} \text{ m}^{-3}$$

$$\frac{h}{\sqrt{3mk_BT}} \left(\frac{N}{V}\right)^{1/3} = \frac{6.22 \times 10^{-34} \text{ J}\cdot\text{s}}{(3 \times 6.64 \times 10^{-27} \text{ kg} \times 1.38 \times 10^{23} \text{ J/K} \times 273 \text{ K})^{1/2}} \times 1.21 \times 10^6 \ \frac{1}{\text{m}} \ll 1$$

YES!

(b) Can it be used for liquid He at T = 4.2 K? The density of liquid He at this temperature is 0.124 g/cm^3

$$\frac{N}{V} = 1.87 \times 10^{28} \text{ m}^3$$

$$\frac{h}{\sqrt{3mk_BT}} \left(\frac{N}{V}\right)^{1/3} = 4.39$$

NO!

Fermi-Dirac Distribution Function: Electron Gas in Metals

Metals. Introduction

Key feature

Metals are good conductors of electric current, indicating that charge carriers (electrons) are free to move around throughout the volume of the material.

Model

gas of electrons
(that is: non-interacting electrons!)

→   successful in explaining conductivity

→   able to explain the contribution to the heat capacity of metals due to electrons

[Heat capacity at high temperatures for both metals and insulators is 3R per mole (Dulong-Petit law), as if there was no extra contribution due to free electrons in metals.]

Electron Gas

Consider a free 3D particle. The stationary Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad \text{or} \qquad -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Solution $\quad \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}} \quad$ (plane wave)

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 e^{i\mathbf{kr}} \quad = \frac{\hbar^2 k^2}{2m}e^{i\mathbf{kr}} = E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r})$$

where

$$E_{\mathbf{k}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 k^2}{2m}$$

Electron Gas

We are interested in properties of a bulk metal, without discussing any surface effects. Therefore we eliminate the surface by imposing the so-called periodic boundary (or Born-Van Karman) conditions

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

For the plane wave $\quad \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}\quad$ it implies that

$$k_x = \frac{2\pi}{L} n_x$$

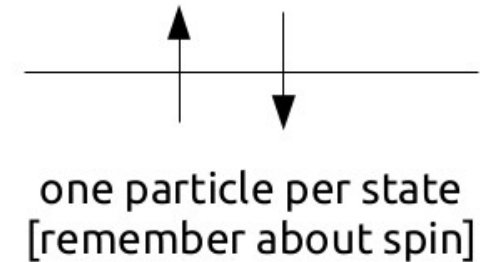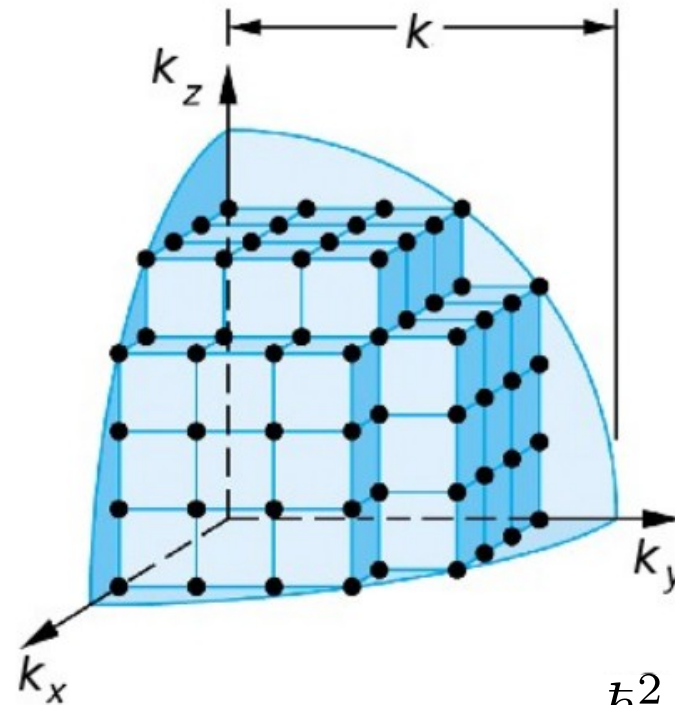$$k_y = \frac{2\pi}{L} n_y \qquad n_x, n_y, n_z = \pm 1, \pm 2, \pm 3, \ldots$$

$$k_z = \frac{2\pi}{L} n_z$$

and

$$E_{\mathbf{k}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{h^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Electron Gas

Illustration of one-particle states available to electrons

one particle per state
[remember about spin]

$$E_{\mathbf{k}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 k^2}{2m}$$

Question: Given a number of electrons, how are the one-particle energy levels being filled? Both at $T = 0$ K and $T > 0$ K. What properties does the system have in these two cases?

Properties of the Electron Gas

Electron Gas. Role of the Temperature

Recall: The electron gas is composed of electrons that are fermions described by the Fermi-Dirac distribution function f_{FD}.

$$f_{\mathrm{FD}}(E) = \frac{1}{Ae^{E/k_BT} + 1} = \frac{1}{e^{(E-\mu)/k_BT} + 1}$$

chemical potential

$$\mu = \mu(T)$$

Note. $f_{\mathrm{FD}}(\mu) = \dfrac{1}{2}$

The value of the chemical potential at $T = 0$ K is called the *Fermi level* (or *Fermi energy*).

$$\mu(0) \overset{\mathrm{def}}{=} E_F$$

Comment

In general, the chemical potential is temperature-dependent, however for the electron gas at temperatures even as high as the room temperature, the temperature correction to the chemical potential is very small, therefore in solid state physics, the chemical potential is commonly referred to as the Fermi level even at $T > 0$ K.

Electron Gas at *T* = 0 K

Fermi-Dirac distribution function at *T* = 0 K

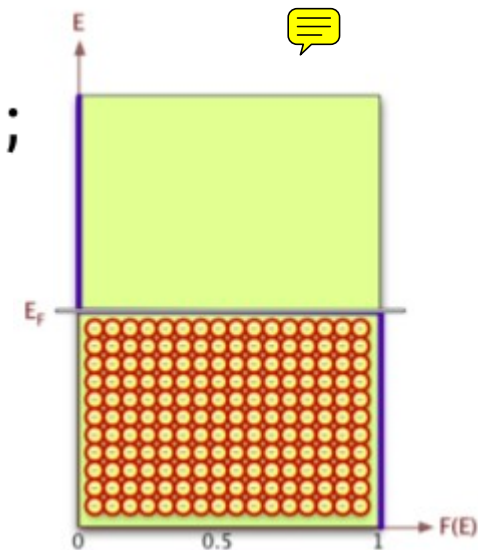$$f_{\text{FD}}(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

$E > E_F$

$$f_{FD}(E) \xrightarrow{T \to 0} \frac{1}{e^{+\infty} + 1} = 0$$

$E < E_F$

$$f_{FD}(E) \xrightarrow{T \to 0} \frac{1}{e^{-\infty} + 1} = 1$$

Interpretation: all states with energy $E < E_F$ occupied; all states with energy $E > E_F$ empty
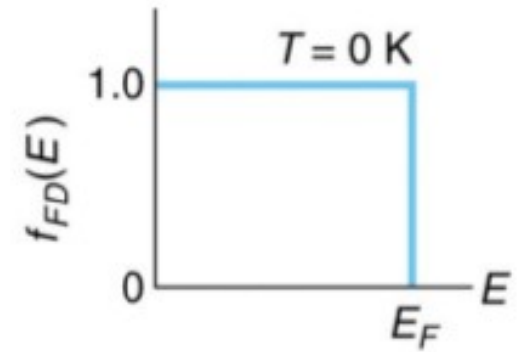
Fermi level E_F – the highest energy level (state) occupied by electrons at *T* = 0 K

Electron Gas at $T = 0$ K. The Fermi Temperature

Given the **Fermi energy**, the corresponding temperature scale (**Fermi temperature**) may be defined as

$$T_F = \frac{E_F}{k_B}$$

Element	Fermi Energy [eV]	Fermi Temperature x 10^4 [K]
Na	3.24	3.77
K	2.12	2.46
Cu	7.00	8.16
Ag	5.49	6.38
Au	5.53	6.42
Fe	11.1	13.0
Hg	7.13	8.29
Al	11.7	13.6

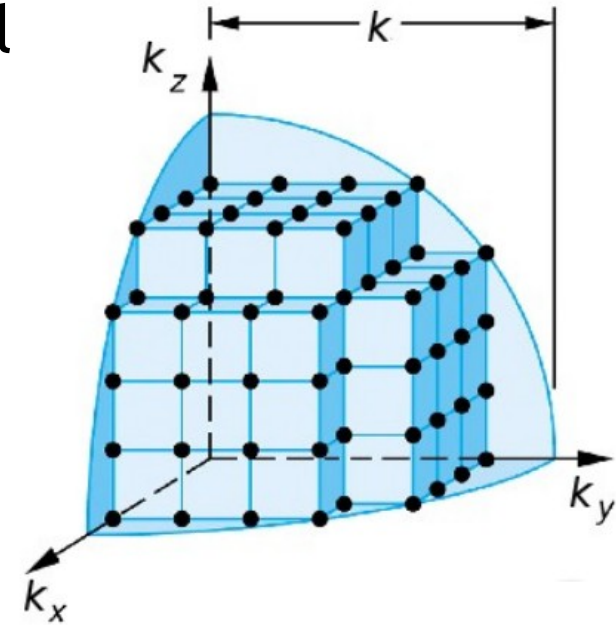N.W. Ashcroft, N.D. Mermin, *Solid State Physics*

3DEG. Degeneracy and Density of States

Energy levels in the 3D electron gas (3DEG) model

$$E = E_{\mathbf{k}} = \frac{\hbar^2}{2m} \left(k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2 k^2}{2m}$$

where the periodic boundary conditions require that

$$k_i = \frac{2\pi}{L}\, n_i, \qquad i = x, y, z$$

Volume in the **k**-space "occupied" by a single level

$$\left(\frac{2\pi}{L} \right)^3 = \frac{(2\pi)^3}{V}$$

Hence, the number of states in the sphere of radius *k*, centered at the origin

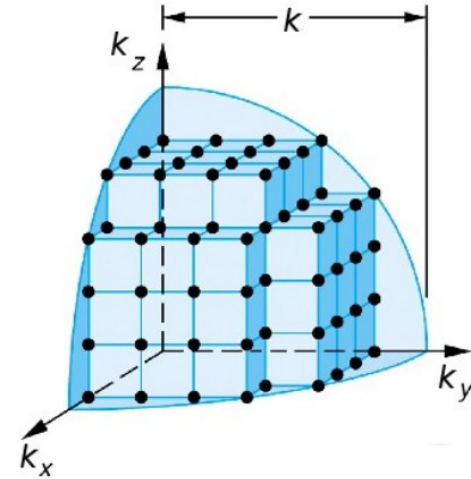$$N_k = 2 \times \frac{\frac{4}{3}\pi k^3}{\frac{(2\pi)^3}{V}}$$

two possible
orientations of spin

3DEG. Density of States

$$N_E = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

Note. In particular, for the Fermi energy, all states for $E < E_F$ are filled and $N_{EF} = N$ (number of electrons), so that

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

Observation. The Fermi energy increases with increasing concentration (density) of electrons as $(N/V)^{2/3}$.

Number of states with energy from the interval (E, E+dE)

$$dN_E = \boxed{\frac{dN_E}{dE}}\, dE = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}\, dE \boxed{\propto \sqrt{E}\, dE}$$

density of states $g(E)$

Observation. The density of one-particle states for the 3D electron gas is proportional to the square root of energy.

Average Energy of Electron in Electron Gas

The average energy of a single electron in the electron gas is found as

$$\langle E \rangle = \frac{1}{N} \int_0^\infty E n(E)\, dE$$

where $n(E)$ is the number of electrons with energy from $(E, E+dE)$

$$n(E) = g(E) f_{FD}(E)$$

density of states
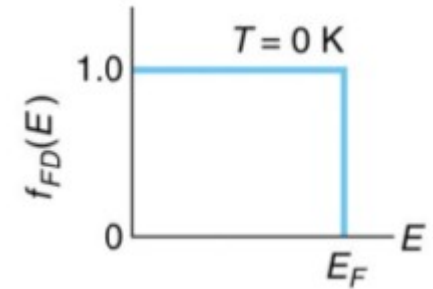(# states with
energy E available)

probability that
the state with E
is occupied
(depends on T)

Recall that in 3DEG $\qquad g(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$

Average Energy of Electron in 3DEG at $T = 0$ K

All states with $E < E_F$ occupied, all other empty

$$\langle E \rangle = \frac{1}{N} \int_0^\infty E g(E) f_{FD}(E)\, dE =$$

$$= \frac{1}{N} \int_0^{E_F} E g(E)\, dE = \frac{1}{N} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{E_F} E^{3/2}\, dE =$$

$$= \frac{1}{N} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{5} E_F^{5/2} = \underbrace{\frac{1}{N} \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}}_{N} \frac{3}{5} E_F = \frac{3}{5} E_F$$
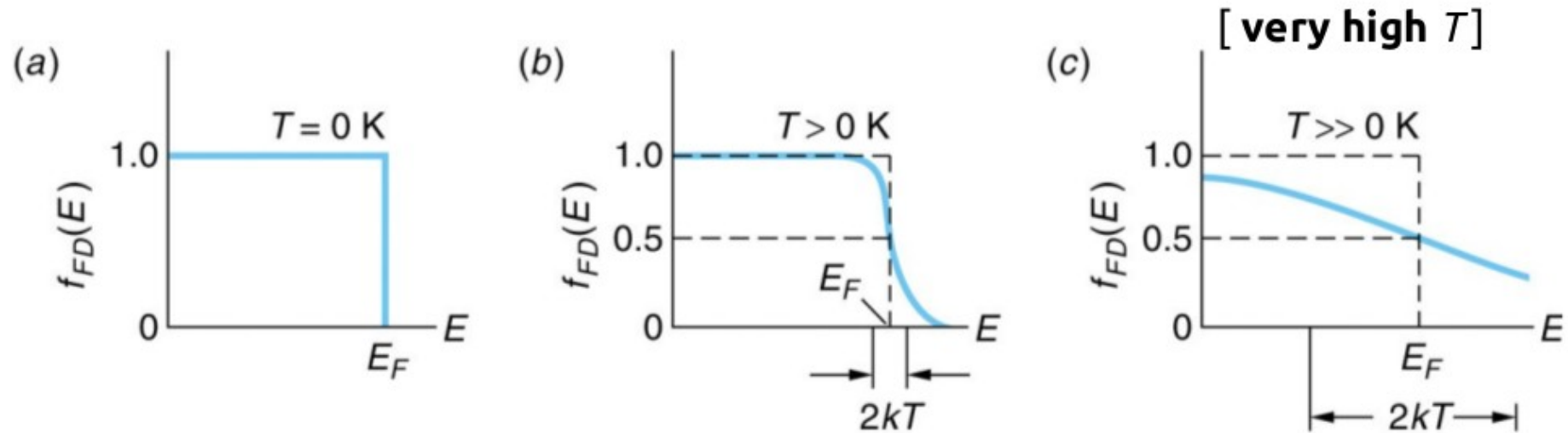
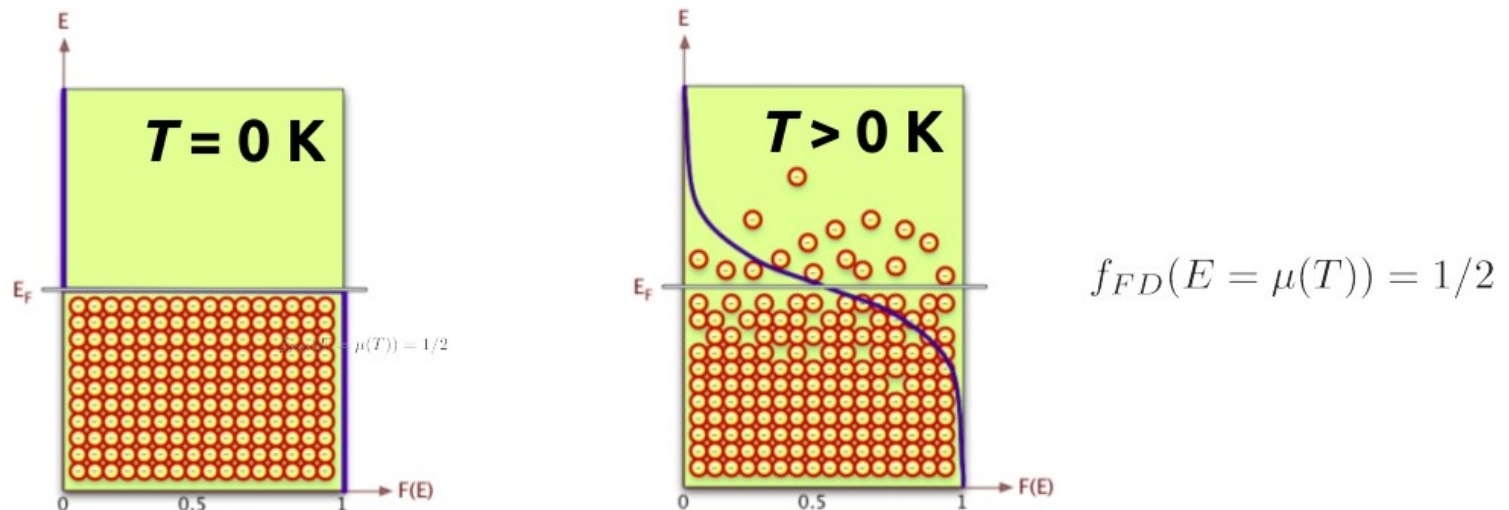$$\boxed{\langle E \rangle = \frac{3}{5} E_F}$$

Implication: At $T=0$ K, the pressure of the electron gas is not zero!

3D Electron Gas at $T > 0$ K

Fermi-Dirac distribution function depends on the temperature

For $T > 0$ K some electrons are excited to previously unoccupied states above the Fermi level, leaving empty states below it.
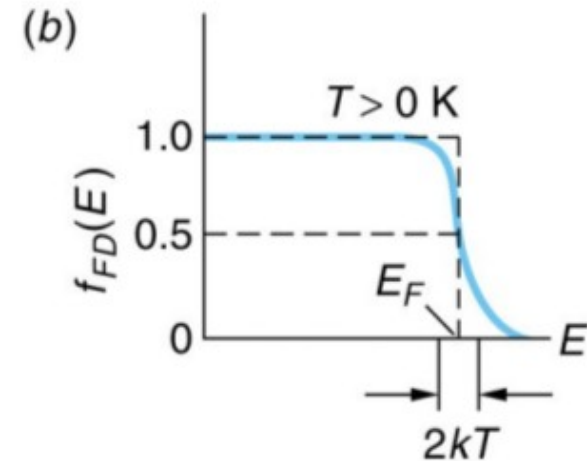

$$f_{FD}(E = \mu(T)) = 1/2$$

3D Electron Gas at $T > 0$ K

The average energy is still found as,

$$\langle E \rangle = \frac{1}{N} \int_0^\infty E g(E) f_{FD}(E)\, dE$$

however f_{FD} is not a step function anymore.

(b)

Consequently, the heat capacity of the 3DEG (per particle) can be found

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{N} \int_0^\infty E g(E) \frac{\partial f_{FD}(E)}{\partial T}\, dE$$
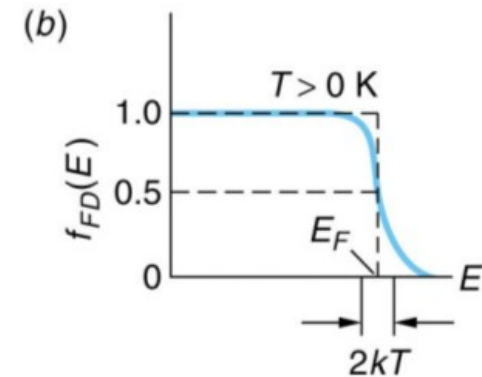
Noticing that the derivative is sharply peaked around the Fermi level, the integral can be eventually evaluated and the molar heat capacity can be found as

$$C_V = \frac{\pi^2}{2} \underbrace{k_B N_A}_{R} \frac{T}{T_F} \propto T$$

Comment on the Heat Capacity of 3DEG

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{N} \int_0^\infty E g(E) \frac{\partial f_{FD}(E)}{\partial T} \, dE$$

sharply peaked
around the Fermi level

(b)

$T > 0$ K

$f_{FD}(E)$

1.0

0.5

E_F

0

E

$2kT$

Implication: The specific heat (and almost all other properties) of metals are determined by a small fraction (of the order of T/T_F) of electrons with energies close to the Fermi level.

Recall that $T_F \sim 10^4$ K. For the room temperature $T \sim 300$ K and $T/T_F \sim 1/100$.

Hence only a small fraction (~1%) of electrons can be excited above the Fermi level. Therefore their contribution to the specific heat (per mole) is only a small fraction of (3/2) R. That explains that there is no significant difference between the heat capacity of metals and insulators at high temperatures, which is 3 R (the law of Dulong-Petit) and is due to the atoms of the crystal lattice.

At low temperatures,

lattice vibrations (phonons)

$$C_V = AT^3 + \gamma T$$

electrons

i.e. the contribution due to electrons dominates.

Summary

Summary

- Whenever the wavelengths of de Broglie waves of identical particles are of the order the distance between the particles, the particles are indistinguishable and quantum distribution functions must be used.

- Many properties of metals are surprisingly well described by the electron gas model and turn out to be determined be a small fraction of electrons around the Fermi level.