Prof Fink's Notes:
The Free Electron Gas Fermi Statistics

Gas of N independent electrons in a volume V (assuming periodic boundary conditions)

I] The system

N electrons in a box of side L such that $V = L^3$

II] Hamiltonian

$$\hat{H}\left(\vec{r}_1,\vec{r}_2,...\vec{r}_N\right) = -\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^{\,2} = \sum_{i=1}^{N}\hat{H}_i$$

III] Eigenvalues and eigenfunctions,

$$\hat{H}_i u_k\left(x,y,z\right) = E_k u_k\left(x,y,z\right)$$

$$u_k\left(x,y,z\right) = u_k\left(\vec{r}\right) = \frac{1}{V^{1/2}}e^{i\vec{k}\cdot\vec{r}}$$

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

Important comment: recall that the functional form of the dispersion relation for the free particle is *parabolic* the discussion is relevant to other cases where the bands have a parabolic shape.

III] Boundary condition: Born Von-Karman

$$u_k\left(x+L,y,z\right) = u_k\left(x,y,z\right)$$

$$u_k\left(x,y,z+L\right) = u_k\left(x,y,z\right)$$

$$u_k\left(x,y+L,z\right) = u_k\left(x,y,z\right)$$

The k vector in this case is the momentum and the energy eigenfunctions are correspondingly momentum eigenfunctions.

$$\hat{P}u_k\left(\vec{r}\right) = \frac{\hbar}{i}\vec{\nabla}u_k\left(\vec{r}\right) = \hbar\vec{k}u_k\left(\vec{r}\right)$$

we can also interpret the vector as a wave vector

$$\left|\vec{k}\right| = \frac{2\pi}{\lambda}$$

where λ is the de-Broglie wavelength.

The application of the boundary condition leads to the following identities,

$$e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1$$

which in turn lead to quantization of the k vectors

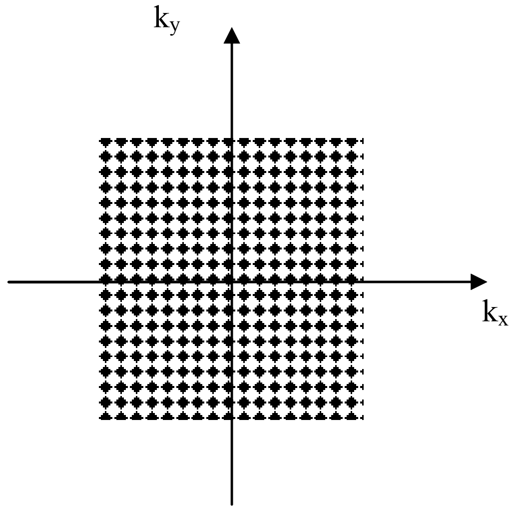
$$k_x = \frac{2\pi n_x}{L} \text{ (same for y and z)}$$

$$\varepsilon_k = \frac{\hbar^2\left(2\pi\right)^3\left(n_x^2+n_y^2+n_z^2\right)}{2mL^2}$$

Enumerating the states

(2D k_x-k_y plot introduction to k space – just an efficient way to display information)

The number of allowed points is just the volume of the k space divided by the volume occupied per point.



The region of k space of volume Ω will contain N allowed k points or spatial states:

$$N_{spatial\ states} = \frac{\Omega}{\left(\frac{2\pi}{L}\right)^2} = \left(\frac{L}{2\pi}\right)^2 \Omega = DOS \times area$$

the factor

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

can be interpreted as the density of spatial states in k space.

Side: A many electron wavefunction of the free electron eigenstates using the Slater determinant:

$$\psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots \vec{r}_N\right) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{k_1}\left(\vec{r}_1\right) & \ldots & u_{k_1}\left(\vec{r}_N\right) \\ & & \\ u_{k_N}\left(\vec{r}_1\right) & & \end{vmatrix}$$

The process of identifying the combination of N, free electron eigenstates needed to produce the lowest possible energy configuration involves choosing the lowest energy k's first and then choosing eigenfunctions associated with higher energies. The resulting volume occupied by the set of chosen k's for a large number of electrons is approximately a sphere, We are now going to introduce N electrons into the system at T=0 and are going to ask what states are these electrons going to occupy? If there are many electrons they will fill a circle in 2D or a sphere in 3D, the surface of this sphere represents the electrons which have the maximum energy, and also separates filled from unfilled states and is called the Fermi surface.

Definitions

Fermi sphere – the surface in k space that separates occupied from unoccupied levels.

Fermi momentum - $\vec{p}_F = \hbar \vec{k}_F$

Fermi velocity - $\frac{\vec{p}_F}{m}$ plays a role in metals similar to that of the thermal velocity in a classical gas.

In 3D:

$$N_{electrons} = 2\frac{4\pi k_F^3}{3}\cdot\frac{1}{\left(\frac{2\pi}{L}\right)^3} = 2\frac{4\pi k_F^3}{3}\frac{V}{\left(2\pi\right)^3} \rightarrow n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

All of these quantities depend on a <u>single parameter</u> the density of the free electrons

Typical values for the free electron densities in metals are:

$$Li = 4.7\times 10^{22}\left[\frac{elec}{cm^3}\right]$$

$$K = 1.3\times 10^{22}\left[\frac{elec}{cm^3}\right]$$

$$Ag = 5.86\times 10^{22}\left[\frac{elec}{cm^3}\right]$$

$$Fe = 17\times 10^{22}\left[\frac{elec}{cm^3}\right]$$

The corresponding de-Broglie wavelength is on the order on angstroms

The Fermi velocity is about 0.01c where c is the speed of light.

The Fermi energy is

$$\varepsilon_F = \frac{\hbar^2}{2m}k_F^2$$

typically in the range of 1.5-15eV

To calculate the ground state energy E, of N electrons,

$$E = 2\sum_{k\le k_F}\frac{\hbar^2}{2m}k^2$$

where all of the states are explicitly counted. Because of the small spacing in the k space it is also possible to transform to a continuous variable and integrate.

$$E = \int_{k<k_F}\underbrace{d^3k\frac{V}{8\pi^3}}_{\substack{\#\text{ of states in volume}\\ d^3k}}\frac{\hbar^2}{2m}k^2 = \frac{V}{\pi^2}\frac{\hbar^2 k_F^5}{10m}$$

The energy per electron in the ground state (using the expression for N/V from above),

$$\frac{E}{N} = \frac{3}{5}\varepsilon_F \rightarrow T_F \approx 10^4 K$$

Density of Levels

A very useful number is the density of states (DOS) function it tells us how many states are located between energies $\varepsilon \rightarrow \varepsilon + d\varepsilon$?

How is this number found?

First it is important to realize that $\varepsilon\left(\vec{k}\right) = \varepsilon$ represents a surface of constant energy.

Once we have a surface how do we calculate the volume enclosed between $\varepsilon \rightarrow \varepsilon + d\varepsilon$?

For the free electron case

$$N = 2\frac{4\pi k^3}{3}\cdot\frac{1}{\left(\frac{2\pi}{L}\right)^3} = \left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}\frac{V}{3\pi^2} = N\left(\varepsilon\right)$$

The density of states function is defined as,

$$\frac{dN}{d\varepsilon} = g\left(\varepsilon\right) = \frac{m}{\hbar^2\pi^2}\sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

The number of one-electron levels in the energy range of $\varepsilon \rightarrow \varepsilon + d\varepsilon$ per unit volume is:

$$g\left(\varepsilon\right)d\varepsilon$$

In general the density of states in a particular band is given by:

$$g_n\left(\varepsilon\right) = \frac{1}{4\pi^3}\int_{S_n(\varepsilon)}\frac{dS}{\left|\vec{\nabla}_k\varepsilon\left(k\right)\right|}$$

$$g\left(\varepsilon\right) = \sum_n g_n\left(\varepsilon\right)$$

It used for calculating thermodynamic quantities:

$$U = \int d\varepsilon g\left(\varepsilon\right)f\left(\varepsilon\right)\varepsilon$$

Statistics of Gases

Classical gas implies distinguishable particles which obey Maxwell-Boltzman statistics

$$\psi(1,2)=\phi_\alpha(1)\phi_\beta(2)$$

Particles with half integral values of the total spin angular momentum – Fermions or electrons – obey Fermi-Dirac statistics

$$\psi(1,2,3,..i,....j,...N)=-\psi(1,2,3,..j,....i,...N)$$

for the simple 2 particle case

$$\psi_A\left(\underbrace{1}_{x_1},\underbrace{2}_{x_2}\right)=\frac{1}{\sqrt{2}}\left(\phi_\alpha(1)\phi_\beta(2)-\phi_\beta(1)\phi_\alpha(2)\right)$$

Particles with integral values of total spin angular momentum – Bosons photons – obey Bose Einstein statistics

$$\psi(1,2,3,..i,....j,...N)=\psi(1,2,3,..j,....i,...N)$$

$$u_S(x_1,x_2)=\frac{1}{\sqrt{2}}\left(\phi_\alpha(1)\phi_\beta(2)+\phi_\beta(1)\phi_\alpha(2)\right)$$

to illustrate why this happens lets consider a simple case of a 2 particle gas A and B which are identical in a system which has 3 possible energy eigenstates s=1, 2 and 3.
The Maxwell-Boltzman case:

	1	2	3
1	AB		
2		AB	
3			AB
4	A	B	
5	A		B
6		A	B
7	B	A	
8	B		A
9		B	A

The Bose Einstein case:

	1	2	3
1	AA		
2		AA	
3			AA
4	A	A	
5	A		A
6		A	A

The Fermi-Dirac case:

	1	2	3
1	A	A	
2	A		A
3		A	A

The number of different possible states for the whole gas:
MB=9, BE=6, FD=3

We can define the following parameter which characterizes the tendency of the particles to "bunch":

$$\xi = \frac{\text{probability of two particles in the same state}}{\text{probability of two particles in different states}}$$

$\xi_{MB} = \frac{1}{2},\ \xi_{BE} = 1,\ \xi_{FD} = 0$

Compared to the classical case the bosons tend to bunch while fermions (electrons) remain apart.

Gas of N identical particles in a volume V in equilibrium with a thermal reservoir at temperature T

Definitions:

s – single particle eigenstate

ε_s - single particle energy eigenvalues

n_s - the number of particles in eigenstate s called the occupation number.

S – an eigenstate (sometimes called a microstate) of the entire gas described once the eigenstate of each particle is given.

E_S – The energy eigenvalues for an eigenstate of the entire gas

Assume we have in our system 3 states s, and two electrons what are the possible "microstates"?

	s=1	s=2	s=3
S=1	A	A	
S=2	A		A
S=3		A	A

What are the properties of this gas:

(1) Total energy of the gas in an eigenstate S:

$$E_S = n_1\varepsilon_1 + n_2\varepsilon_2 + ... = \sum_S n_s\varepsilon_s$$

$$\sum_i n_i = N$$

(2) It can be shown that the probability of finding the system in a particular eigenstate S of energy E_s is given by:

$$P(S) = \frac{e^{-\frac{E_S}{k_B T}}}{\sum_{\text{all } S} e^{-\frac{E_S}{k_B T}}}$$

where the denominator is a very useful function called the partition function

$$Z = \sum_{\text{all } S} e^{-\frac{E_S}{k_B T}}$$

The partition function Z is related to the Helmholtz free energy of the system through

$$F = -kT \ln Z$$

the summation is over all distinct states of the gas – S (i.e. all possible values of $(n_1, n_2, ..., n_N)$) this expression holds for all types of particles the difference lies in the number of different states S.

The chemical potential is defined as the change in free energy upon adding a particle to the system:

$$\mu \equiv F(N+1) - F(N) = \frac{\partial F}{\partial N}$$

All thermodynamic properties of the gas can be calculated from the knowledge of Z.

Fermi-Dirac statistics

range of allowable single-electron state occupation number

$$n_s = 0,1$$

since the particles are indistinguishable it is enough to use the occupation vector $\{n_1, n_2, ...\}$ to completely define a state

How is this different from the classical gas Maxwell-Boltzmann statistics?

the allowable values of $n_s = 0,1,2,3.....,N$

furthermore since the particles are considered to be distinguishable it is not sufficient to provide the occupation vector $\{n_1, n_2, ...\}$ one needs to consider which particles are in each single particle state and separately count all of the different possibilities.

The most profound difference between the different particle types is when considering the gas at T=0 or at the ground state. Assume that the lowest single particle energy eigenvalues is ε_1 the lowest possible energy state of the many electron system is very different for the electron and classical gas cases we just discussed….

A very important quantity is the mean number of particles in a particular single electron state s, for electrons:

$$\overline{n}_s = \begin{pmatrix} \text{sum of the probabilities of} \\ \text{obtaining gas states S where} \\ \text{single-electron state s, is occupied} \end{pmatrix}$$

Using the partition function defined above one can show that

$$\overline{n}_s = \frac{1}{e^{\frac{(\varepsilon_s - \mu)}{kT}} + 1}$$

This relation (for fermions) is called the Fermi-Dirac distribution it plays a key role in determining electronic properties.

An important observation regarding the FD distribution:

$$n_s \xrightarrow{\varepsilon_s \to \infty} 0$$

$$n_s \le 1$$

which is a result of Pauli's exclusion principle

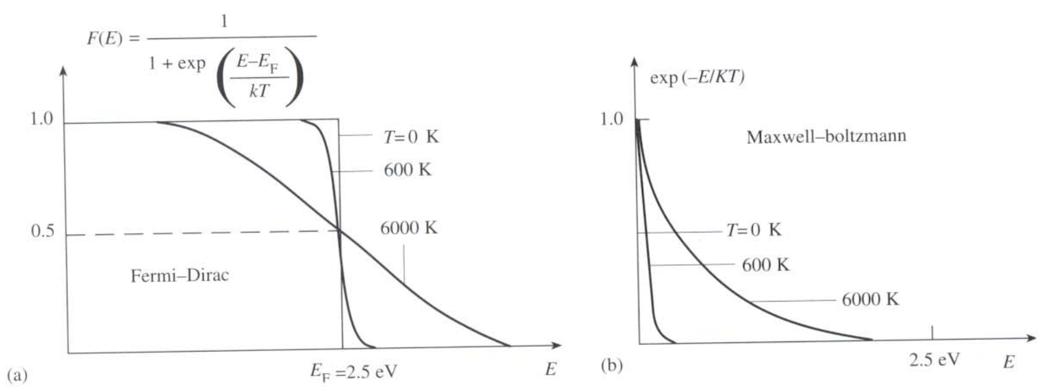


Fig. 6.1
(a) The Fermi–Dirac distribution function for a Fermi energy of 2.5 eV and for temperatures of 0 K, 600 K, and 6000 K.
(b) The classical Maxwell–Boltzmann distribution function of energies for the same temperatures.

A slightly different view on the Fermi Dirac Distribution

The properties of an N particle system which is in thermal equilibrium at temperature T should be calculated by averaging over all N particle eigenstates where each state of energy ε is weighted by

$$P(\varepsilon) = \frac{e^{-\varepsilon/k_B T}}{\sum_{all\ states} e^{-\varepsilon_i/k_B T}}$$

The denominator is called the partition function and is related to the Helmholtz free energy.

$$e^{-F/k_BT} = \sum_{all\ states} e^{-\varepsilon_i/k_BT}$$

The probability of having a particular 1 electron level with energy – ε occupied by an electron is just,

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}$$

One can derive this probability by considering that it is nothing else but the sum of independent probabilities of having a particular energy level occupied

$$f(\varepsilon) = \sum_{\substack{\text{summation} \\ \text{over all states - }\alpha \\ \text{where there is} \\ \text{an electron in} \\ \text{level E}}} P_\alpha(\varepsilon)$$

It is also useful to note that the sum of all occupation numbers should equal the number of electrons in the system

$$N = \sum_{all\ states} f_i(\varepsilon)$$

The chemical potential at temperature T is defined as the difference in free energies upon adding an additional particle to the system

$$\mu = F_{N+1} - F_N$$

the chemical potential has a weak temperature dependence and is sometimes called the Fermi Energy

Does this occupation probability function reproduce the ground state occupation?

$$f_{\vec{k},s} = \begin{cases} 1 & \varepsilon(\vec{k}) < \varepsilon_F \\ 0 & \varepsilon(\vec{k}) > \varepsilon_F \end{cases}$$

which is exactly what is recovered at the limit of T approaching 0 from the occupation function

$$\lim_{T\to 0} f_{\vec{k},s} = \begin{cases} 1 & \varepsilon(\vec{k}) < \varepsilon_F \\ 0 & \varepsilon(\vec{k}) > \varepsilon_F \end{cases}$$

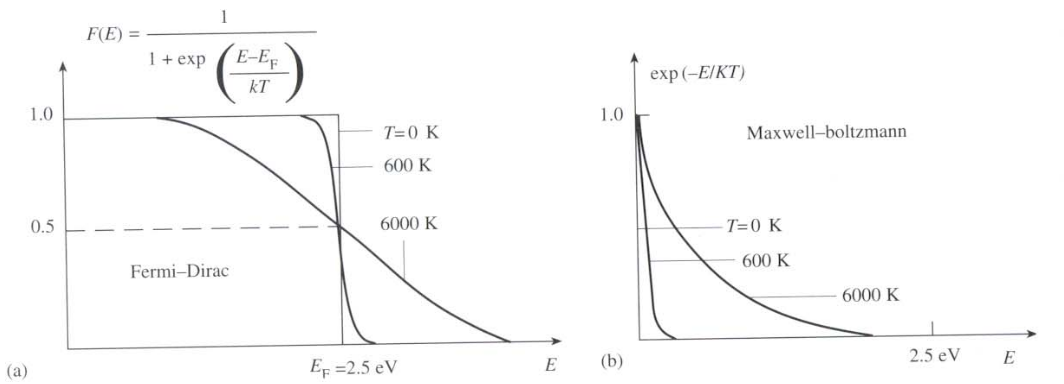


Fig. 6.1
(a) The Fermi–Dirac distribution function for a Fermi energy of 2.5 eV and for temperatures of 0 K, 600 K, and 6000 K.
(b) The classical Maxwell–Boltzmann distribution function of energies for the same temperatures.

We can use this function to evaluate different average quantities of the gas for example, The total energy of the system at temperature T,

$$U = 2\sum_{\substack{all\ states \\ k}} \varepsilon\left(\vec{k}\right) f\left(\varepsilon\left(\vec{k}\right)\right)$$

The energy density is given by,

$$u = \frac{U}{V} = \int \underbrace{d^3k \frac{1}{4\pi^3} f\left(\varepsilon\left(\vec{k}\right)\right)}_{\substack{\#\text{ of occupied} \\ \text{states in volume } d^3k}} \frac{\hbar^2}{2m} k^2$$

The density of states function is defined as,

$$g(\varepsilon) = \frac{m}{\hbar^2\pi^2}\sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

and the number of one-electron levels in the energy range of $\varepsilon \to \varepsilon + d\varepsilon$ per unit volume is:

$$g(\varepsilon)d\varepsilon$$

$$u = \int_0^\infty d\varepsilon g(\varepsilon) f(\varepsilon)\varepsilon$$

$$n = \int_0^\infty d\varepsilon g(\varepsilon) f(\varepsilon)$$

The heat capacity of the free electron gas

The heat capacity of an electron gas:

The equipartition theorem basically states that for each degree of freedom in the Hamiltonian there is a contribution of 1/2k to the heat capacity. Therefore it is expected that the free electron gas will have a heat capacity of:

$$c_v = n\frac{3}{2}k_B$$

yet in reality the contribution of the free electrons to the heat capacity was only 0.01 of that value? The basic paradox was how were the electrons mobile enough to participate in the conduction process yet did not contribute to the heat capacity?

When we heat the sample from T=0K not every electron gains $k_B T$ as expected from classical considerations – in fact only the electrons near the Fermi energy can absorb that extra kinetic energy by promoting themselves to higher energy orbitals. The rest of the electrons are trapped in their orbitals.

The fraction of electrons that can be excited is on the order of $\frac{T}{T_F}$

$$c_v = \frac{\pi^2}{2}\frac{k_B T}{\varepsilon_F} n k_B$$