

Fermi gases

Gabriel T. Landi

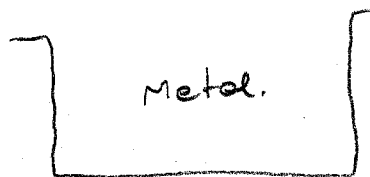
References:

- Salinas, chapter 9
- Ashcroft, chapter 2.

The ground state of a free electron gas

By far, the most important type of Fermi gas is a metal. In a metal, the electrons are weakly bound to the ions and may therefore move almost freely through the crystal. Their only constraint is that they cannot leave the metal: there is a potential barrier for escaping (this is the work function that you study in the context of the photoelectric effect).

thus, to a first approximation, we may treat electrons in a metal as simply particles in a box.



If the electron is ever excited to a sufficiently high energy state, it may eventually be removed from the box, as in the photoelectric effect. But if we assume no such processes take place, then we may assume the potential well is infinite. This is what we will do here.

Since electrons are Fermions we therefore reach the following conclusion:

"Electrons in a metal \approx a Fermi gas in a box"

This is what we are going to assume in these notes. But before we start doing calculations, I have two comments to make.

The first is about lattice vibrations. We have already seen that the ions in a solid may vibrate around their equilibrium position. This should have some influence on the electrons. And it does. For instance, they are responsible for superconductivity and many other phenomena.

Superconductivity = attractive $e^- - e^-$ interaction mediated by phonons

However, to see this interaction we usually need to go to specific conditions, such as very low temperatures. If we look at the behavior of simple metals, such as Au, Ag, Cu, etc., and if we don't go to very low temperatures, then the electron-phonon interaction may be neglected, at least to first order.

My second comment is about electron-electron interactions. The e^- are charged particles and therefore repel each other. This interaction is not negligible. However, it turns out that ignoring it is not always too bad. An interacting electron gas is called a Fermi liquid. And it turns out that the properties of Fermi liquids are not so very different from those of a Fermi gas. We will therefore neglect the $e^- - e^-$ Coulomb interaction

Here: neglect electron-phonon and electron-electron interactions

There is, however, one thing we cannot ignore: that the electrons are indistinguishable particles and therefore obey the Pauli exclusion principle. This means that two electrons cannot occupy the same quantum state.

For electrons in a box the quantum states are of the form

$$j = (k, \sigma)$$

$$k_i = \frac{2\pi l_i}{L}, \quad l_i = 0, \pm 1, \pm 2, \dots \quad (1)$$

$$\sigma = \pm 1$$

$$E_k = \frac{\hbar^2 k^2}{2m}$$

Let us now understand how the Pauli principle affects the ground state of the system.

Suppose our box has 1 electron. The ground state then corresponds to placing this single electron in the lowest energy state, which is that with $k = (0, 0, 0)$.

$$g_s: \downarrow e^- @ (0, 0, 0, \pm 1) \quad E = 0$$

Since there is no magnetic field, $\sigma = +1$ and $\sigma = -1$ are degenerate, so it does not matter in which state we put the electron.

Now consider two electrons. We construct the g.s. as

$$g_s: (0, 0, 0, 1), (0, 0, 0, -1), \quad E = 0$$

Finally, if we put a third electron, then we can no longer fill the state with zero momentum. So we have no choice but to place the third electron at one of

$$\left(\frac{2\pi}{L}, 0, 0, \pm 1\right), \left(0, \frac{2\pi}{L}, 0, \pm 1\right), \left(0, 0, \frac{2\pi}{L}, \pm 1\right)$$

All 6 states are degenerate and have an energy $\epsilon = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}\right)^2$.

You now see that, if we continue like this, a system with N electrons will have N occupied levels, in order of increasing energy.

The number N of electrons is actually determined by the type of atom in your metal. For instance, Au has a valency $z=1$, meaning that each Au atom contributes 1 electron to the gas. The other electrons in the Au atom remain bounded to the nucleus. Combining this with the density of Au, we then obtain an electron density of $n = 5.9 \times 10^{22}$ electrons/cm³. That is, a crystal of 1 cm³ volume will have $N = 5.9 \times 10^{22}$ electrons, which will gradually fill all energy states, as discussed above.

We saw in the previous notes that as long as

$$n = \frac{N}{V} \ll \frac{1}{\lambda^3} \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}} \quad (2)$$

that the gas would behave classically. For Au we have, at $T=300\text{K}$,

$$\lambda \approx 4.3 \times 10^{-7} \text{ cm. Hence}$$

$$\frac{1}{\lambda^3} \approx 1.25 \times 10^{19} \text{ 1/cm}^3$$

This is certainly not larger than 10^{22} . Conclusion: for an electron gas quantum effects are essential even at room temperature.

free kinetic theory to this "gas" of conduction electrons of mass m , which the molecules of an ordinary gas) move against a background of heavy ions. The density of the electron gas can be calculated as follows:

The element contains 0.6022×10^{24} atoms per mole (Avogadro's number) per cm^3 , where ρ_m is the mass density (in grams per cubic centimeter), atomic mass of the element. Since each atom contributes Z electrons, of electrons per cubic centimeter, $n = N/V$, is

$$n = 0.6022 \times 10^{24} \frac{Z\rho_m}{A} \quad (1.1)$$

shows the conduction electron densities for some selected metals, typically of order 10^{22} conduction electrons per cubic centimeter, varying from 10^{22} for cesium up to 24.7×10^{22} for beryllium.⁵ Also listed in Table 1 is a widely used measure of the electronic density, r_s , defined as the radius of a sphere whose volume is equal to the volume per conduction electron.

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3}; \quad r_s = \left(\frac{3}{4\pi n} \right)^{1/3} \quad (1.2)$$

where r_s both in angstroms (10^{-8} cm) and in units of the Bohr radius $a_0 = 0.529 \times 10^{-8}$ cm; the latter length, being a measure of the radius of an atom in its ground state, is often used as a scale for measuring atomic sizes. Note that r_s/a_0 is between 2 and 3 in most cases, although it ranges between 1 and 2 for the alkali metals (and can be as large as 10 in some metallic compounds). The densities are typically a thousand times greater than those of a classical gas at room temperatures and pressures. In spite of this and in spite of the strong temperature and electron-ion electromagnetic interactions, the Drude model of electron and electron-ion interactions by the methods of the kinetic theory of dilute gas, with only slight modifications. The basic assumptions are these:

1. In collisions the interaction of a given electron, both with the other electrons and with the ions, is neglected. Thus in the absence of externally applied electric fields each electron is taken to move uniformly in a straight line. In the presence of externally applied fields each electron is taken to move as determined by the laws of motion in the presence of those external fields, but neglecting the complicated fields produced by the other electrons and ions.⁶ The independent electron-electron interactions between collisions is known as the *independent electron approximation*. The corresponding neglect of electron-ion interactions is known as the *free electron approximation*. We shall find in subsequent chapters that

the range for metallic elements under normal conditions. Higher densities can be attained by increasing the pressure (which tends to favor the metallic state). Lower densities are found in com-

pressures, the electron-ion interaction is not entirely ignored, for the Drude model implies that the electrons are confined to the interior of the metal. Evidently this confinement is not by their attraction to the positively charged ions. Gross effects of the electron-ion and electron interaction like this are often taken into account by adding to the external fields a suitably chosen field representing the average effect of the electron-electron and electron-ion interactions.

FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS^a

ELEMENT	Z	n ($10^{22}/\text{cm}^3$)	r_s (Å)	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn (α)	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

^a At room temperature (about 300 K) and atmospheric pressure, unless otherwise noted. The radius r_s of the free electron sphere is defined in Eq. (1.2). We have arbitrarily selected one value of Z for those elements that display more than one chemical valence. The Drude model gives no theoretical basis for the choice. Values of n are based on data from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963.

although the independent electron approximation is in many contexts surprisingly good, the free electron approximation must be abandoned if one is to arrive at even a qualitative understanding of much of metallic behavior.

2. Collisions in the Drude model, as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron. Drude attributed them to the electrons bouncing off the impenetrable ion cores (rather than to electron-electron collisions, the analogue of the predominant collision mechanism in an ordinary gas). We shall find later that electron-electron scattering is indeed one of the least important of the several scattering mechanisms in a metal, except under unusual conditions. However,

The Fermi level

We define the Fermi level as the highest occupied state after filling all levels with the N electrons.

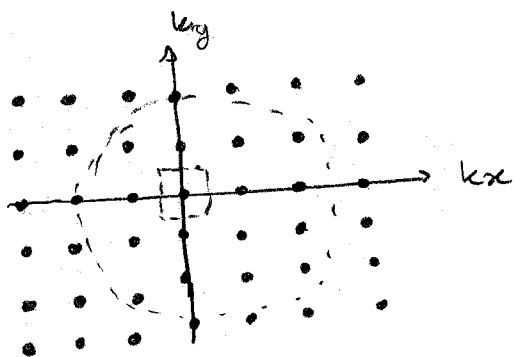
Fermi level = highest occupied state

Fermi momentum = k_F = highest occupied momentum

Fermi energy = E_F = highest occupied energy.

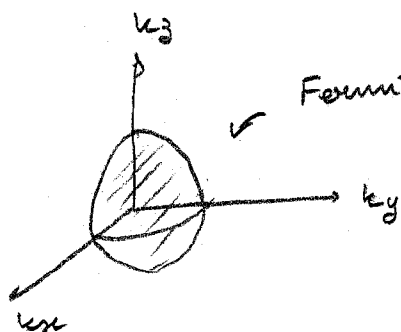
Let us now determine the Fermi level. We will do that in two ways. First, we will do it by brute force, so that you gain some intuition. Then we will do it in a more automated way using the density of states.

The values of k are discrete and we fill them in increasing order



← Imagine this in 3D!

In 3D we will fill all k values inside a certain sphere. The filling will not be perfect since the points are discrete. But the k_i are very finely spaced and N is really large, so we may imagine we are filling a smooth sphere. The radius of this sphere is the Fermi momentum k_F . This is called the Fermi surface



Fermi surface = surface in momentum space.

The volume of the sphere is $\frac{4\pi k_F^3}{3}$. But since the k are discrete we can also imagine the sphere as a bunch of tiny cubes. Recall that

$$k_i = \frac{2\pi l_i}{L}$$

thus, the volume of each cube is

$$\Delta k_x \Delta k_y \Delta k_z = \left(\frac{2\pi}{L}\right)^3$$

If there are N electrons, then we can fill 2 electrons per cube (because of spin $\sigma = \pm 1$). Thus, we will occupy in total $N/2$ cubes, which implies a volume

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

Comparing the 2 volumes we get

$$\frac{4\pi k_F^3}{3} = \frac{N}{V} \frac{8\pi^3}{2}$$

or

$$k_F^3 = 3\pi^2 N/V$$

we therefore conclude that the Fermi momentum depends only on the electron density $n = N/V$.

$$k_F = (3\pi^2 n)^{1/3}, \quad n = \frac{N}{V}$$

(3)

Once we know the Fermi momentum, we may determine the Fermi energy as

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad (4)$$

we may also determine other quantities of interest. For instance, since momentum is $\hbar k$ and velocity is p/m , we may define the Fermi velocity as

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{1/3} \quad (5)$$

this gives a rough measure of the typical velocities of the electrons in the highest occupied states.

Similarly, we may define the Fermi temperature, as

$$k_B T_F = E_F \quad (6)$$

this gives a rough measure of the temperature at which the electron gas would behave classically. For all metals, $T_F \sim 10^4 \text{K}$, meaning that only at 10000K they would behave classically. But this is way above the melting point of the solid. Conclusion: electrons in a metal must always be treated quantum mechanically. Always.

Table 2.1
FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND
FERMI VELOCITIES FOR REPRESENTATIVE METALS^a

ELEMENT	r_s/a_0	ϵ_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm ⁻¹	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

^a The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 9.11 \times 10^{-28}$ grams.

assumes that the electronic energy per unit volume in a 1-cm cube of copper is the same as in a 2-cm cube).

Using (2.29) to evaluate (2.27), we find that the energy density of the electron gas is:

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{k < k_F} dk \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \quad (2.30)$$

To find the energy per electron, E/N , in the ground state, we must divide this by $N/V = k_F^3/3\pi^2$, which gives

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \epsilon_F \quad (2.31)$$

We can also write this result as

where T_F , the Fermi temperature, is

$$T_F = \frac{\epsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \text{ K.}$$

Note, in contrast to this, that the energy per electron in a classical ideal gas vanishes at $T = 0$ and achieves a value as large as (2.32) only at $T = \frac{2}{3} T_F$. Given the ground-state energy E , one can calculate the pressure of an electron gas from the relation $P = -(\partial E/\partial V)_N$. Since $E = \frac{3}{5} N \epsilon_F$ and is proportional to k_F^2 , which depends on V only through a factor $n^{2/3} = (N/V)^{2/3}$ that¹⁶

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

One can also calculate the compressibility, K , or bulk modulus, $B = -V \frac{\partial P}{\partial V}$, by:

$$B = \frac{1}{K} = -V \frac{\partial P}{\partial V}$$

Since E is proportional to $V^{-2/3}$, Eq.(2.34) shows that P varies as $V^{-5/3}$, and

$$B = \frac{5}{3} P = \frac{10}{9} \frac{E}{V} = \frac{2}{3} n \epsilon_F$$

or

$$B = \left(\frac{6.13}{r_s/a_0} \right)^5 \times 10^{10} \text{ dynes/cm}^2$$

In Table 2.2 we compare the free electron bulk moduli (2.37) calculated with the measured bulk moduli, for several metals. The agreement for alkali metals is fortuitously good, but even when (2.37) is substantially c

Table 2.2
BULK MODULI IN 10^{10} DYNES/CM² FOR SOME
TYPICAL METALS^a

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

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

The Density of States (DOS)

when working with electrons, the density of states is extremely convenient. Recall that it is defined as

$$\sum_{\mathbf{k}, \sigma} f(\epsilon_{\mathbf{k}}) = \int_0^{\infty} d\epsilon D(\epsilon) f(\epsilon) \quad (7)$$

Let's derive it once again, just for fun:

$$\begin{aligned} \sum_{\mathbf{k}, \sigma} f(\epsilon_{\mathbf{k}}) &= 2 \sum_{\mathbf{k}} f(\epsilon_{\mathbf{k}}) = 2 \frac{V}{(2\pi)^3} \int d^3k f(\epsilon_{\mathbf{k}}) \\ &= 2 \frac{V}{(2\pi)^3} 4\pi \int dk k^2 f(\epsilon_{\mathbf{k}}) \end{aligned}$$

Now change variables to $\epsilon = \frac{\hbar^2 k^2}{2m}$. We get

$$\begin{aligned} k &= \sqrt{\frac{2m}{\hbar^2}} \sqrt{\epsilon} \quad \Rightarrow \quad dk = \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2\sqrt{\epsilon}} d\epsilon \\ \Rightarrow k^2 dk &= \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{\sqrt{\epsilon} d\epsilon}{2} \end{aligned}$$

thus

$$\sum_{\mathbf{k}, \sigma} f(\epsilon_{\mathbf{k}}) = \frac{2 \cdot 8\pi V}{(4\pi)^3} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{2} \int d\epsilon \sqrt{\epsilon} f(\epsilon)$$

thus

$$D(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}$$

(8)

With the DOS we may now compute the Fermi energy as

$$\int_0^{E_F} dE D(E) = N \quad (9)$$

Let's check:

$$\begin{aligned} \int_0^{E_F} dE D(E) &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{E_F} dE \sqrt{E} \\ &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3} E_F^{3/2} \\ &= N \end{aligned} \quad (10)$$

Thus

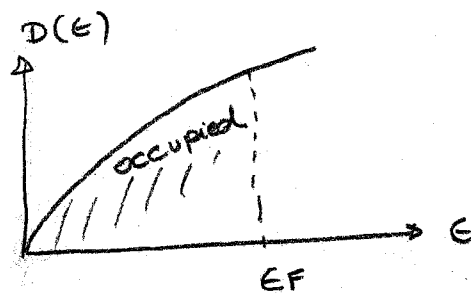
$$E_F^{3/2} = 3\pi^2 N/V \left(\frac{\hbar^2}{2m}\right)^{3/2}$$

or

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

which is Eq (4).

The rationale is made clearer by having the following picture in mind



Using Eq (10) we may also write the DOS in a more convenient way:

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

and

$$D(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon}$$

Thus

$$D(\epsilon) = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon} \Rightarrow D(\epsilon_F) = \frac{3N}{2\epsilon_F} \quad (11)$$

Now let's compute the total energy of the system:

$$U = \int_0^{\epsilon_F} d\epsilon D(\epsilon) \epsilon \quad (12)$$

this is the internal energy at zero temperature. We have

$$U = \frac{3N}{2\epsilon_F^{3/2}} \int_0^{\epsilon_F} d\epsilon \epsilon^{3/2} = \frac{3N}{2\epsilon_F^{3/2}} \frac{2}{5} \epsilon_F^{5/2}$$

thus

$$U = \frac{3}{5} N \epsilon_F \quad (13)$$

At $T=0$ the average energy of each electron is $\frac{3}{5} \epsilon_F$.

Naively, we could think that it should be $\frac{1}{2} \epsilon_F$ since all states up to ϵ_F are filled. But the density of states is not uniform; it increases as $\sqrt{\epsilon}$, meaning that there are more states with higher energy. Consequently, when we average we get $3/5 = 0.6$ instead of 0.5 .

Pressure and bulk modulus

In the previous set of notes we showed that, for a quantum gas in the canonical ensemble, both Bosonic and Fermionic, it is always true that

$$pV = \frac{2}{3} U \quad (14)$$

we may use this formula to estimate the pressure produced by the electron gas on the solid. We get

$$\begin{aligned} p &= \frac{2}{3} \frac{U}{V} = \frac{2}{3V} \frac{1}{5} N E_F \\ &= \frac{2}{5} \frac{N}{V} \frac{\hbar^2}{2m} (3\pi^2 N/V)^{2/3} \end{aligned}$$

thus

$$p = \frac{2}{5} \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \left(\frac{N}{V}\right)^{5/3} \quad (15)$$

An even more interesting quantity is the Bulk modulus

$$B = -V \frac{\partial p}{\partial V} \quad (16)$$

It measures the resistance of a gas to compression [The compressibility is defined as $\kappa = 1/B$].

we get

$$\begin{aligned} B &= -V \frac{2}{5} \frac{\hbar^2}{2m} (3\pi^2)^{2/3} N^{5/3} \left(-\frac{5}{3}\right) V^{-8/3} \\ &= \frac{5}{3} \frac{2}{5} \frac{\hbar^2}{2m} (3\pi^2)^{3/2} \left(\frac{N}{V}\right)^{5/3} \end{aligned}$$

Thus

$$B = \frac{5}{3} P = \frac{5}{3} \frac{2}{3} \frac{U}{V} = \frac{5}{3} \frac{2}{3} \frac{3}{5} \frac{2}{V} \epsilon_F$$

Or

$$B = \frac{2}{3} n \epsilon_F$$

(17)

Below is a comparison between this result and the experimental measurement.

Table 2.2
BULK MODULI IN 10^{10} DYNES/CM² FOR SOME
TYPICAL METALS^a

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

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

As can be seen, both results are of the same order of magnitude. This shows that a substantial part of the compressibility of a solid comes from the electrons and the Pauli principle, a remarkable result. The other part comes from the lattice vibrations and also from the electron-electron interactions.

Fermi gases at finite temperatures

We saw that at $T=0$ all states up to E_F were occupied; the Fermi sphere is filled. At $T \neq 0$ thermal fluctuations will allow some of the electrons to occupy states above the Fermi surface. For $T \neq 0$ the average number of electrons at an energy ϵ will be given by the Fermi-Dirac distribution

$$\bar{n}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad (18)$$

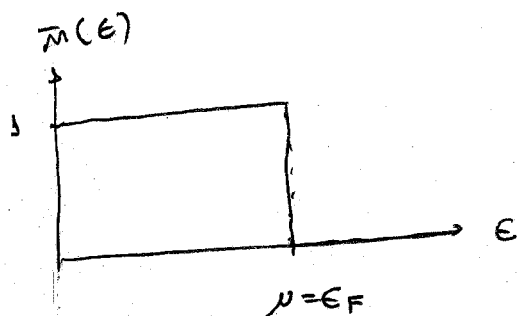
Let's understand the behavior of this function at $T=0$ first. Then we move to $T \neq 0$. For $T \rightarrow 0$ (or $\beta \rightarrow \infty$) we have

$$e^{\beta(\epsilon - \mu)} = \begin{cases} \gg 1 & \text{if } \epsilon > \mu \\ \ll 1 & \text{if } \epsilon < \mu \end{cases} \quad (19)$$

For $\bar{n}(\epsilon)$ this implies that

$$\bar{n}(\epsilon) = \begin{cases} 0 & \text{if } \epsilon > \mu \\ 1 & \text{if } \epsilon < \mu \end{cases} \quad (20)$$

This looks like



It is clear from this analysis that

$$\mu(T=0) = \epsilon_F$$

(21)

For $T \neq 0$ the chemical potential will change, but at $T=0$ it is simply the Fermi energy.

We may also write the Fermi-Dirac distribution as

$$f(\epsilon) = \Theta(\epsilon_F - \epsilon)$$

($T=0$)

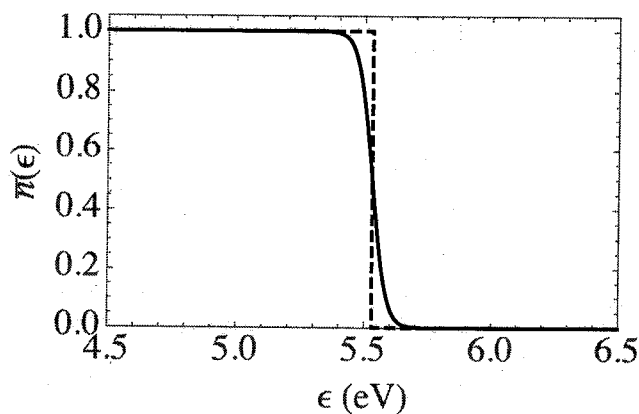
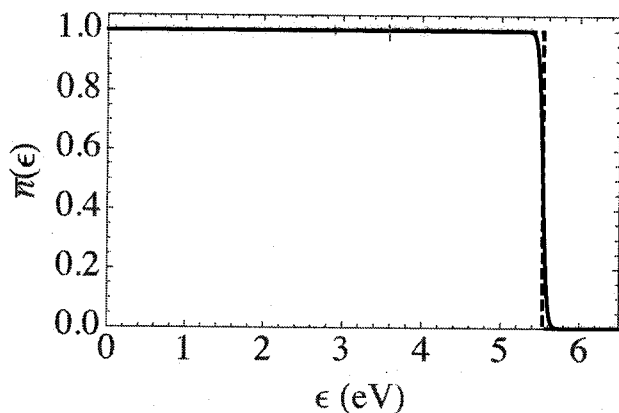
(22)

where $\Theta(x)$ is called the step function, or Heaviside function

$$\Theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases}$$

(23)

Now what about $T \neq 0$. Well, let's assume $T = 300$ K, which gives $k_B T = 0.026$ eV. For concreteness, assume also that $\mu = \epsilon_F(\text{Gold}) = 5.53$ eV. Here is what we find



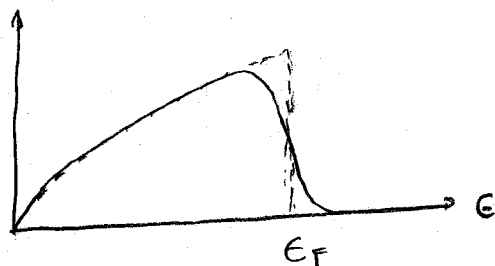
what we see is that at $T=300\text{ K}$, $\bar{n}(\epsilon)$ will differ from $\Theta(\epsilon_F - \epsilon)$ only in the vicinity of the Fermi surface. The electrons deep within the Fermi sphere practically do not feel the effects of the thermal fluctuations. All that the thermal fluctuations do is produce a small cloud of electrons above the Fermi surface.

All thermodynamic formulas are modified simply by introducing $\bar{n}(\epsilon)$; for instance

$$N = \int_0^{\infty} d\epsilon D(\epsilon) \bar{n}(\epsilon) \quad (24)$$

$$U = \int_0^{\infty} d\epsilon D(\epsilon) \epsilon \bar{n}(\epsilon) \quad (25)$$

we may interpret $D(\epsilon)\bar{n}(\epsilon)$ as a thermally weighted density of states



If $\bar{n}(\epsilon) = \Theta(\epsilon_F - \epsilon)$ then

$$N = \int_0^{\infty} d\epsilon D(\epsilon) \Theta(\epsilon_F - \epsilon) = \int_0^{\epsilon_F} d\epsilon D(\epsilon) \quad (26)$$

which is Eq (9).

The most important quantity to compute at finite temperatures is the specific heat

$$C = \frac{1}{N} \frac{\partial U}{\partial T} \quad (27)$$

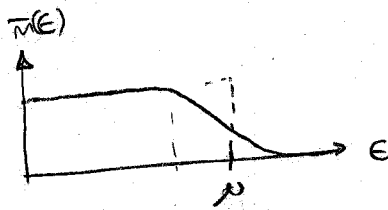
Sommerfeld expansion

Integrals such as (24) and (25) usually cannot be computed analytically because of $\bar{n}(\epsilon)$. But that is not such a big deal since the deviation of $\bar{n}(\epsilon)$ from $\Theta(\epsilon_F - \epsilon)$ is usually small. The Sommerfeld expansion is a way of expanding $\bar{n}(\epsilon)$ at low temperatures.

The mathematics of the Sommerfeld expansion is not so easy, but the idea is. Consider an integral of the form

$$\int_0^{\infty} d\epsilon f(\epsilon) \bar{n}(\epsilon) d\epsilon \quad (28)$$

We have already seen that $\bar{n}(\epsilon)$ differs only slightly from $\Theta(\epsilon_F - \epsilon)$:



It will not carry out the Sommerfeld expansion here. It is done in all detail in Appendix C of Ashcroft and Mermin. The result is

$$\int_0^{\infty} f(\epsilon) \bar{n}(\epsilon) d\epsilon \approx \int_0^{\mu} f(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 f'(\mu) \quad (29)$$

If $T \rightarrow 0$ then $\mu \rightarrow \epsilon_F$ and we recover all zero temperature results, such as (26)

Now let us apply the Sommerfeld expansion to (24) and (25):

$$N = \int_0^{\infty} d\epsilon D(\epsilon) \bar{n}(\epsilon) \approx \int_0^{\mu} d\epsilon D(\epsilon) + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) \quad (30)$$

$$U = \int_0^{\infty} d\epsilon D(\epsilon) \epsilon \bar{n}(\epsilon) \approx \int_0^{\mu} d\epsilon D(\epsilon) \epsilon + \frac{\pi^2}{6} (k_B T)^2 [D(\mu) + \mu D'(\mu)] \quad (31)$$

Now we need to be careful with the difference between ϵ_F and μ . For instance, we have seen that

$$N = \int_0^{\epsilon_F} d\epsilon D(\epsilon) \quad (32)$$

But this does not mean that

$$N \approx \int_0^{\mu} d\epsilon D(\epsilon) \quad (\text{Wrong!})$$

These are two different things. In fact, we will learn in a second that

$$\mu \approx \epsilon_F - \alpha (k_B T)^2$$

where $\alpha > 0$ is a constant.

Let us then be careful and do our expansions so that they always come out correct to order $(k_B T)^2$. This means that

$$\frac{\pi^2}{6} (k_B T)^2 D'(\mu) \approx \frac{\pi^2}{6} (k_B T)^2 D'(\epsilon_F)$$

and

$$\frac{\pi^2}{6} (k_B T)^2 [\mu D'(\mu) + D(\mu)] \approx \frac{\pi^2}{6} (k_B T)^2 [\epsilon_F D'(\epsilon_F) + D(\epsilon_F)]$$

In these terms we may safely replace μ by ϵ_F since any corrections will be of order higher than $(k_B T)^2$.

what we need to be careful about are the integrals. We may write

$$\int_0^{E_F} f(\epsilon) d\epsilon = \int_0^{\mu} f(\epsilon) d\epsilon + \int_{\mu}^{E_F} f(\epsilon) d\epsilon$$

We assume E_F and μ are close to each other so we may approximate

$$\int_{\mu}^{E_F} f(\epsilon) d\epsilon \approx (E_F - \mu) f\left(\frac{E_F + \mu}{2}\right)$$

where the function was evaluated midway through the interval.

But

$$f\left(\frac{E_F + \mu}{2}\right) = f\left(E_F - \frac{\alpha}{2}(k_B T)^2\right) \approx f(E_F) - \frac{\alpha}{2}(k_B T)^2 f'(E_F)$$

Retaining only terms up to order $(k_B T)^2$ we then get

$$\int_{\mu}^{E_F} f(\epsilon) d\epsilon \approx (E_F - \mu) f(E_F) - \underbrace{\frac{(E_F - \mu) \alpha}{2} (k_B T)^2 f'(E_F)}_{\sim (k_B T)^2} \approx (k_B T)^4$$

conclusion

$$\int_{\mu}^{E_F} f(\epsilon) d\epsilon \approx (E_F - \mu) f(E_F)$$

and, therefore

$$\int_0^{\mu} f(\epsilon) d\epsilon \approx \int_0^{E_F} f(\epsilon) d\epsilon + (\mu - E_F) f(E_F) \quad (33)$$

Returning now to (30) and (31) we get

$$N \approx \int_0^{\epsilon_F} d\epsilon D(\epsilon) + (\mu - \epsilon_F) D(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\epsilon_F) \quad (34)$$

$$U \approx \int_0^{\epsilon_F} d\epsilon D(\epsilon) \epsilon + (\mu - \epsilon_F) \epsilon_F D(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 [D(\epsilon_F) + \epsilon_F D'(\epsilon_F)] \quad (35)$$

From (34), because of Eq (32) we conclude that

$$N = N + (\mu - \epsilon_F) D(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\epsilon_F)$$

Solving for μ :

$$\mu = \epsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{D'(\epsilon_F)}{D(\epsilon_F)} \quad (36)$$

This shows, as anticipated, that the first correction to μ is of the order $(k_B T)^2$.

Now we look at (35). Recall that, from Eq (13)

$$\int_0^{\epsilon_F} D(\epsilon) \epsilon d\epsilon = \frac{3}{5} N \epsilon_F$$

We then get

$$U \approx \frac{3}{5} N \epsilon_F + \underbrace{\epsilon_F \left\{ (\mu - \epsilon_F) D(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\epsilon_F) \right\}}_{= 0 \text{ because of (36)}} + \frac{\pi^2}{6} (k_B T)^2 D(\epsilon_F)$$

Thus we finally conclude that

$$U = \frac{3}{5} N E_F + \frac{\pi^2}{6} (k_B T)^2 D(E_F) \quad (37)$$

The heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{\pi^2}{3} k_B^2 T D(E_F) \quad (38)$$

so the specific heat will be

$$c = \frac{C}{N} = \frac{\pi^2 k_B^2}{3} T \frac{D(E_F)}{N} \quad (39)$$

From (11) we had that $D(E_F) = \frac{3N}{2E_F}$. Thus

$$c = \frac{\pi^2 k_B^2}{3} T \frac{3}{2} \frac{N}{E_F} \frac{1}{N}$$

we may then write

$$c = \gamma T \quad \gamma = \frac{\pi^2 k_B^2}{2E_F} \quad (40)$$

the electronic contribution to the specific heat is linear in T . The constant γ is called the Sommerfeld coefficient. If you measure γ experimentally you may infer the Fermi energy of the material.