Fermi Dirac statistics: free electron of metal

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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Here we discuss the Fermi-Dirac statistics of free electrons in metals at 0 K.

1. Density of states

In free electron Fermi gas model, the Density of states is expressed by

$$D(\varepsilon)d\varepsilon = 2\frac{V}{(2\pi)^3}4\pi k^2 dk = \frac{V}{\pi^2}k^2 dk$$

where the energy dispersion of electron is given by

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

We note that

$$k = \sqrt{\frac{2m}{\hbar^2}}\sqrt{\varepsilon} \qquad dk = \sqrt{\frac{2m}{\hbar^2}}\frac{1}{2\sqrt{\varepsilon}}d\varepsilon$$

Then the density of states can be rewritten as

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

or

$$D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon} \qquad \text{(Density of states)}$$

2. Fermi energy, Fermi wave-number, and Fermi velocity

The number of electrons is given by

$$N = \int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon$$
$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\varepsilon} f(\varepsilon) d\varepsilon$$
$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon$$
$$= \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\varepsilon_F\right)^{3/2}$$

where $f(\varepsilon) = 1$ for $\varepsilon < \varepsilon_F$ and 0 for $\varepsilon > \varepsilon_F$. Then the Fermi energy is obtained as

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

where n is the number density; $n = \frac{N}{V}$. The Fermi temperature is defined by

$$T_F = \frac{\varepsilon_F}{k_B}.$$

The Fermi wave number is

$$k_F = \left(3\pi^2 n\right)^{1/3}$$

The Fermi velocity is given by

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

((**Note**))

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

$$N = a\int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon = \frac{2a}{3} {\varepsilon_F}^{3/2}$$

where

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

Thus we have

$$D(\varepsilon_F) = \frac{3N}{2\varepsilon_F}.$$

3. Internal energy and average energy

The internal energy is given by

$$U = \int_0^\infty \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon$$
$$= \int_0^\infty \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{3/2} f(\varepsilon) d\varepsilon$$

The total number is

$$N = \int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon$$

Then we have the ratio as

$$\frac{U}{N} = \frac{\int_0^\infty \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon}{\int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon}$$

At $T = 0$K, we have

$$\frac{U}{N} = \frac{\int_0^{\varepsilon_F} \varepsilon\sqrt{\varepsilon} d\varepsilon}{\int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon} = \frac{\frac{2}{5}\varepsilon_F^{5/2}}{\frac{2}{3}\varepsilon_F^{3/2}} = \frac{3}{5}\varepsilon_F$$

or

$$U = \frac{3}{5} N \varepsilon_F = \frac{3}{5} N \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{2/3} = \frac{3}{10} \frac{N\hbar^2}{m} \left(3\pi^2 n\right)^{2/3}$$

The pressure P:

$$P = -\left(\frac{\partial U}{\partial V}\right) = \frac{3}{5} \frac{\hbar^2}{m} (3\pi^2)^{2/3} \left(\frac{N}{V}\right)^{5/3} = \frac{2U}{3V}$$

or

$$P = \frac{2}{3V} \frac{3}{5} N \varepsilon_F = \frac{2}{5} n \varepsilon_F$$

Since

$$\ln P = \ln[\frac{3}{5} \frac{\hbar^2}{m} (3\pi^2)^{2/3}] + \frac{5}{3} (\ln N - \ln V)$$

the bulk modulus B is

$$\begin{aligned} B &= -V \frac{\partial P}{\partial V} \\ &= -PV \frac{\partial \ln P}{\partial V} \\ &= -PV \frac{\partial}{\partial V} (-\frac{5}{3} \ln V) \\ &= \frac{5}{3} P \\ &= \frac{5}{3} \frac{2}{3} \frac{U}{V} \\ &= \frac{10}{9} \frac{U}{V} \end{aligned}$$

or

$$B = \frac{10}{9} \frac{3}{5} \frac{N \varepsilon_F}{V} = \frac{2}{3} n \varepsilon_F$$

4. Numerical calculations

(a) Cu

face-centered cubic (fcc) with a lattice constant a = 3.597 Å.

There are 4 Cu atoms per cubic lattice (conventional) with the volume a^3. Each Cu atom has one conduction electron.

$$n = \frac{4}{a^3} = 8.59486 \text{ x } 10^{23} \text{ cm}^{-3}$$

The Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = 1.13782 \text{ x } 10^{-11} \text{ erg} = 7.10171 \text{ eV}$$

The Fermi wave number:

$$k_F = \left(3\pi^2 n\right)^{1/3} = 1.36527 \text{ x } 10^{8} \text{ /cm}$$

The Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = 1.58955 \text{ x } 10^{8} \text{ cm/s}$$

The Fermi temperature:

$$T_F = 8.2411 \text{ x } 10^{4} \text{ K.}$$

The pressure:

$$P = \frac{2}{5} n\varepsilon_F = 39.1776 \text{ G Pa}$$

Note that in the classical theory the pressure is $P_0 = nk_B T$. Since $\varepsilon_F = k_B T_F$, the ratio P/P_0 is

$$\frac{P}{P_0} = \frac{2}{5}\frac{T_F}{T}.$$

The bulk modulus:

$$B = \frac{2}{3} n\varepsilon_F = 65.1959 \text{ GPa}$$

where the experimental value is 123 GPa,

GPa=10^9 Pa. Pa=N/m^2=10 dyne/cm^2
1 atm = 1.01325 x 10^5 Pa.

(b) Al

face-centered cubic (fcc) with a lattice constant a = 4.046 Å.

There are 4 Al atoms per cubic lattice (conventional) with the volume a^3. Each Al atom has three conduction electrons (trivalent).

$$n = \frac{4 \times 3}{a^3} = 1.81177 \text{ x } 10^{23} \text{ cm}^{-3}$$

The Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = 1.87061 \text{ x } 10^{-11} \text{ erg} = 11.6754 \text{ eV}$$

The Fermi wave number:

$$k_F = \left(3\pi^2 n\right)^{1/3} = 1.75055 \text{ x } 10^8 \text{ /cm}$$

The Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = 2.02657 \text{ x } 10^8 \text{ cm/s}$$

The Fermi temperature:

$$T_F = 1.35488 \text{ x } 10^5 \text{ K.}$$

The pressure:

$$P = \frac{2}{5} n\varepsilon_F = 1.35565 \text{ x } 10^{11} \text{ Pa}$$

The bulk modulus:

$$B = \frac{2}{3} n\varepsilon_F = 225.941 \text{ GPa}$$

where the experimental value is 76 GPa.

(c) Na

Body-centered cubic (bcc) with a lattice constant a = 4.225 Å.

There are 2 Na atoms per cubic lattice (conventional) with the volume a^3. Each Na atom has one conduction electron.

$$n = \frac{2}{a^3} = 2.65054 \text{ x } 10^{22} \text{ cm}^{-3}$$

The Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = 5.19362 \text{ x } 10^{-12} \text{ erg} = 3.2416 \text{ eV}$$

The Fermi wave number:

$$k_F = \left(3\pi^2 n\right)^{1/3} = 9.22398 \text{ x } 10^7 \text{ /cm}$$

The Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = 1.06684 \text{ x } 10^8 \text{ cm/s}$$

The Fermi temperature:

$$T_F = 3.7617 \text{ x } 10^4 \text{ K.}$$

The pressure:

$$P = \frac{2}{5} n\varepsilon_F = 5.50635 \text{ G Pa}$$

The bulk modulus:

$$B = \frac{2}{3} n\varepsilon_F = 9.18486 \text{ GPa}$$

where the experimental value is 6.3 GPa.

(d) K (potassium)

Body-centered cubic (bcc) with a lattice constant a = 5.225 Å.

There are 2 K atoms per cubic lattice (conventional) with the volume a^3. Each P atom has one conduction electron.

$$n = \frac{2}{a^3} = 1.40207 \text{ x } 10^{22} \text{ cm}^{-3}$$

The Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = 3.39699 \text{ x } 10^{-12} \text{ erg} = 2.12024 \text{ eV}$$

The Fermi wave number:

$$k_F = \left(3\pi^2 n\right)^{1/3} = 7.45986 \text{ x } 10^7 \text{ /cm}$$

The Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = 8.6361 \text{ x } 10^7 \text{ cm/s}$$

The Fermi temperature:

$$T_F = 2.4604 \text{ x } 10^4 \text{ K.}$$

The pressure:

$$P = \frac{2}{5} n\varepsilon_F = 1.90514 \text{ G Pa}$$

The bulk modulus:

$$B = \frac{2}{3} n\varepsilon_F = 3.17523 \text{ GPa}$$

where the experimental value is 3.1 GPa.

(e) Lithium (Li)

Body-centered cubic (bcc) with a lattice constant a = 3.51 Å.

There are 2 Li atoms per cubic lattice (conventional) with the volume a^3. Each Li atom has one conduction electron.

$$n = \frac{2}{a^3} = 4.62497 \text{ x } 10^{22} \text{ cm}^{-3}$$

The Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = 7.52754 \text{ x } 10^{-12} \text{ erg} = 4.69832 \text{ eV}$$

The Fermi wave number:

$$k_F = \left(3\pi^2 n\right)^{1/3} = 1.11048 \text{ x } 10^8 \text{ /cm}$$

The Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = 1.28557 \text{ x } 10^8 \text{ cm/s}$$

The Fermi temperature:

$$T_F = 5.4521 \text{ x } 10^4 \text{ K.}$$

The pressure:

$$P = \frac{2}{5} n\varepsilon_F = 13.92 \text{ G Pa}$$

The bulk modulus:

$$B = \frac{2}{3} n\varepsilon_F = 23.2097 \text{ GPa}$$

where the experimental value is 11 GPa.

(f) Lead (Pb)

fcc with a lattice constant $a = 4.920$ Å.

There are 4 Pb atoms per cubic lattice (conventional) with the volume a^3. Each Pb atom has four conduction electrons.

$$n = \frac{4 \times 4}{a^3} = 1.34346 \text{ x } 10^{23} \text{ cm}^{-3}$$

The Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = 1.53249 \text{ x } 10^{-11} \text{ erg} = 9.56504 \text{ eV}$$

The Fermi wave number:

$$k_F = \left(3\pi^2 n\right)^{1/3} = 1.58446 \text{ x } 10^8 \text{ /cm}$$

The Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = 1.83429 \text{ x } 10^8 \text{ cm/s}$$

The Fermi temperature:

$$T_F = 1.10998 \text{ x } 10^5 \text{ K.}$$

The pressure:

$$P = \frac{2}{5} n\varepsilon_F = 82.3534 \text{ Pa}$$

The bulk modulus:

$$B = \frac{2}{3} n\varepsilon_F = 137.256 \text{ GPa}$$

where the experimental value is 46 GPa.

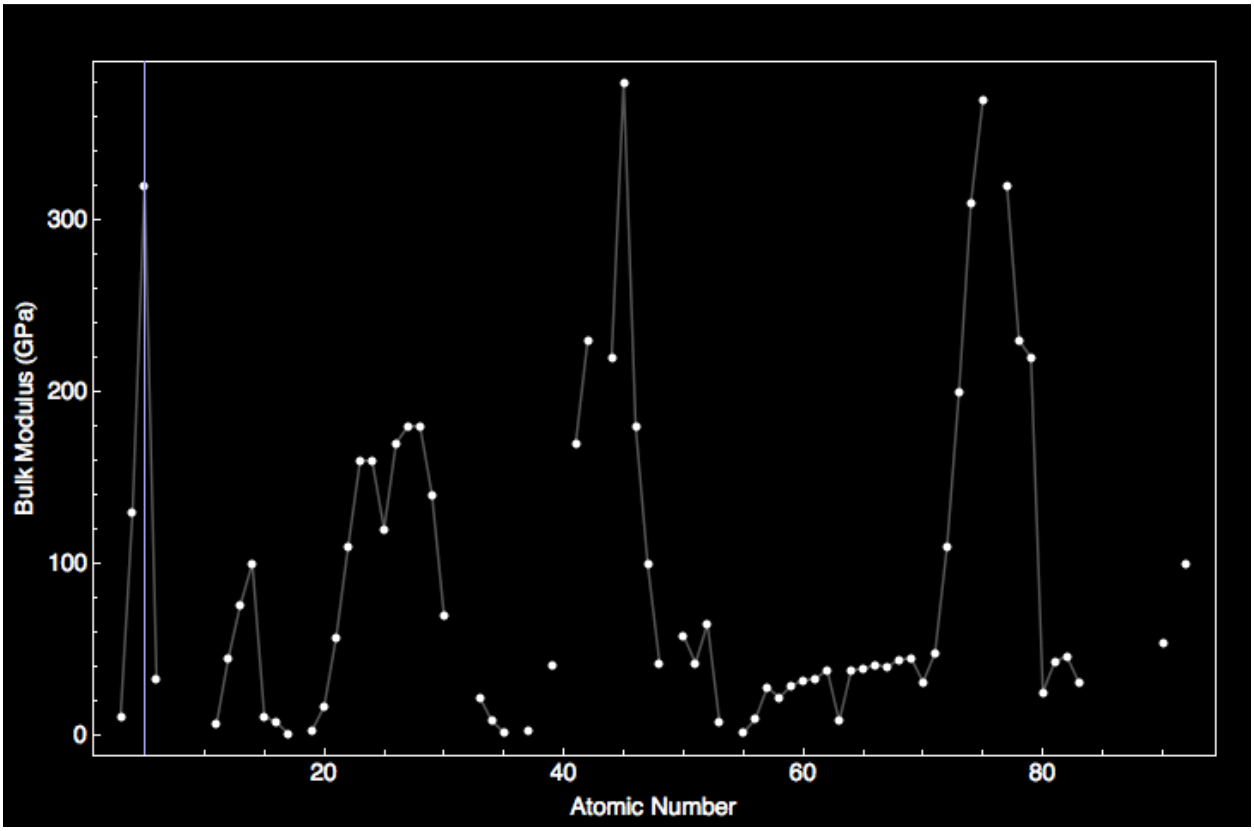

Fig. Bulk modulus vs atomic number. Na (11), Al (13), and K (19), and Cu(29), Pb(82).

((**Summary**))

In summary, the electrons in metals have a very large kinetic energy at 0 K, of the order of the energy that is attained only at such high temperatures in the classical theory. This arises from the Pauli principle, according to which at most two electrons (of opposite spins) cam occupy a state..

Table 6.1. Properties of free-electron metals

Element	Z	n (10^{22} cm^{-3})	k_F (10^8 cm^{-1})	$\mathcal{E}_F$ (eV)	T_F (10^4 K)	v_F (10^8 cm s^{-1})	r_s/a_0
Li	1	4.60	1.11	4.68	5.43	1.28	3.27
Na	1	2.54	0.91	3.15	3.66	1.05	3.99
K	1	1.32	0.73	2.04	2.37	0.85	4.95
Rb	1	1.08	0.68	1.78	2.06	0.79	5.30
Cs	1	0.85	0.63	1.52	1.76	0.73	5.75
Cu	1	8.49	1.36	7.04	8.17	1.57	2.67
Ag	1	5.86	1.20	5.50	6.38	1.39	3.02
Au	1	5.90	1.20	5.53	6.42	1.39	3.01
Be	2	24.72	1.94	14.36	16.67	2.25	1.87
Mg	2	8.62	1.37	7.11	8.26	1.58	2.65
Ca	2	4.66	1.11	4.72	5.48	1.29	3.26
Sr	2	3.49	1.01	3.89	4.52	1.17	3.59
Ba	2	3.15	0.98	3.64	4.22	1.13	3.71
Zn	2	13.13	1.57	9.42	10.93	1.82	2.31
Cd	2	9.26	1.40	7.47	8.66	1.62	2.59
Hg	2	16.22	1.69	10.84	12.59	1.95	2.15
Al	3	18.07	1.75	11.66	13.53	2.02	2.07
Ga	3	15.31	1.65	10.44	12.11	1.92	2.19
In	3	11.50	1.50	8.62	10.01	1.74	2.41
Sn	4	14.83	1.64	10.22	11.86	1.89	2.22
Pb	4	13.19	1.57	9.45	10.97	1.82	2.30
Sb	5	16.54	1.70	10.99	12.75	1.97	2.14
Bi	5	14.04	1.61	9.85	11.43	1.86	2.26
Mn	4	32.61	2.13	17.28	20.05	2.46	1.70
Fe	2	16.90	1.71	11.15	12.94	1.98	2.12
Co	2	18.18	1.75	11.70	13.58	2.03	2.07
Ni	2	18.26	1.76	11.74	13.62	2.03	2.07

Conduction electron density, Fermi wave vector, energy, temperature, Fermi velocity, and radius parameter r_s [Eq. (6.30)] in units of the Bohr radius, a_0, for selected metallic elements computed by assigning each element a number of conduction electrons Z, and treating it as a free-electron gas. Densities are obtained from data of periodic table inside front cover, and are measured at 293 K. Assignments of Z to the four transition metals at end of table are conventional but not obvious.

M.P. Marder, Condensed Matter Physics, second edition (Wiley, 2010).