Solution to Problem 1 and Problem 3 of Homework Set 5.

Problem 1. Consider a free Fermi gas with N electrons. Find the energy of the ground state (ground state means at zero temperature $T = 0$) of the gas as N varies from 1 through 15 (HINT: Note that for small number of particles one cannot convert sums over $\mathbf{k}$ states into integrals, but must instead use explicit enumeration of states in the box with periodic boundary conditions, whose wave vector is $\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ and eigenenergy is $\epsilon_{\mathbf{k}} = \hbar\mathbf{k}^2/2m$).

Problem 3. Consider a thin layer of silver (density of particles $n = 5.86{\cdot}10^{22}$ electrons/cm^3), 10^6 Å wide and 10^6 Å long along the x and y axis, respectively.

(a) Take the layer to be 4.1 Å thick along the z-axis. Treat the layer as a free Fermi gas, demanding that the wave function vanish at the boundaries along the z-axis. Find the difference between the energies of the lowest and highest occupied single-particle states, and compare the difference to the bulk Fermi energy.

(b) Repeat the problem (a) with a layer 8.2 Å thick along the z-axis.

SOLUTIONS: (a) The understand the difference between the filling of single particle energy levels for free (Sommerfeld) electrons in bulk metals and in thin layers made of such metals, we first look at energy levels of single non-interacting electron in a box $L \times L \times L$ with periodic boundary conditions introduced for convenience (the box then fills the space in all three directions while this Born-von Karman procedure eliminates the need to deal with continuous energy spectrum, which can be always recovered by sending $L \to \infty$), as relevant for Problem 1. In this case, the single particle states are labeled by the $\mathbf{k}$ vector

$$\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \tag{1}$$

so that single particle energy levels

$$\varepsilon_{\mathbf{k}}^{\text{box}} = \frac{\hbar^2\mathbf{k}^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(n_x^2 + n_y^2 + n_z^2\right), \tag{2}$$

are labeled by the corresponding quantum numbers $n_x, n_y, n_z = \ldots, -3, -2, -1, 0, 1, 2, 3\ldots$ which can take any integer value. The lowest energy level $\varepsilon^{\text{box}}(n_x, n_y, n_z) = 0$ is specified by $(n_x, n_y, n_z) = (0, 0, 0)$ and can accept two electrons (one spin-$\uparrow$ and one spin-$\downarrow$). The next energy level is six-fold degenerate—there are six states $(1, 0, 0)$, $(-1, 0, 0)$, $(0, 1, 0)$, $(0, -1, 0)$, $(0, 0, 1)$, $(0, 0, -1)$ which can accommodate twelve electrons all having the same energy $\varepsilon^{\text{box}}(n_x, n_y, n_z) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2$. In this case, one increases the quantum numbers n_x, n_y, n_z at the same time in steps of one until all available electrons $n * L^3$ are distributed in the lowest energy levels to form the many-body ground state at $T = 0$. The highest occupied single particle state at $T = 0$ is the Fermi energy ε_F. For example, if we have 15 electrons to distribute as in Problem 1., the highest occupied single particle state would be $\varepsilon^{\text{box}}(1, 1, 0) = 2\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 = \varepsilon_F^{\text{box}}$ and the ground state energy is $\varepsilon_{\text{ground}}^{\text{box}} = 2\varepsilon^{\text{box}}(0, 0, 0) + 12\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 + 2\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 = 56(\hbar^2\pi^2)/(2mL^2)$.

In the case of a thin metal film $L_x = L_y = L_r \gg L_z$, electron motion is confined in the z-direction, which can be simply modeled by requiring that its wave function vanishes at the boundaries along the z-axis (due to approximation of real confining potential by an infinite one at the boundaries so that electron cannot tunnel outside of the layer along the z-axis). At the same time we assume that electrons are free in the xy-plane so that final model to which we apply the Schrödinger equation is that of a thin layer periodically repeated only in the x and y directions. Therefore, the energy spectrum of a single electron in such layer is

$$\varepsilon(n_x, n_y, n_z) = \frac{\hbar^2}{2m}\left[\left(\frac{2\pi}{L_r}\right)^2 (n_x^2 + n_y^2) + \left(\frac{\pi}{L_z}\right)^2 n_z^2\right], \tag{3}$$

where $n_x, n_y = \ldots, -3, -2, -1, 0, 1, 2, 3 \ldots$, while $n_z = 1, 2, \ldots$. The major difference between Eq. (3) and Eq. (2) is that filling of n_z costs much more energy (because of $L_z \ll L_r$) then filling of n_x, n_y states. That is, the lowest energy state is $(0, 0, 1)$, the next one is specified by $(1, 0, 1)$, $(-1, 0, 1)$, $(0, 1, 1)$, $(0, -1, 1)$, and so on. Eventually, for large n_x, n_y we will reach a state $(n_x, n_y, 1)$ whose energy is the same as the state $(0, 0, 2)$. This point, at which states with $n_z = 2$ will start to fill, is, therefore, specified by the condition

$$\varepsilon(n_x, n_y, 1) = \varepsilon(0, 0, 2) \tag{4}$$

$$\frac{\hbar^2}{2m}\left(\frac{2\pi}{L_r}\right)^2 (n_x^2 + n_y^2) + \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2 1^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2 3^2 \tag{5}$$

$$(n_x^2 + n_y^2) = \frac{3L_r^2}{4L_z^2}. \tag{6}$$

The number of electrons which have been distributed into the single-particle energy levels from $(0, 0, 1)$ to $(n_x, n_y, 1)$ is obtained by dividing the number of states in the circle $\pi(k_x^2 + k_y^2)$ with the surface corresponding to single such state $\left(\frac{2\pi}{L_r}\right)^2$ and multiplying this ration by 2 for spin

$$N = \frac{2\pi(k_x^2 + k_y^2)}{4\pi^2/L_r^2} = 2\pi\left(\frac{2\pi}{L_r}\right)^2 (n_x^2 + n_y^2)(4\pi^2/L_r^2)^{-1} = 2\pi(n_x^2 + n_y^2). \tag{7}$$

The actual number of available electrons in the silver film is $nL_r^2 L_z$. If this number is equal or smaller than N in Eq. (7), then all electrons stay in the energy levels with $n_z = 1$, as determined by the condition obtained from Eq. (6) and Eq. (7)

$$n_x^2 + n_z^2 = \frac{nL_r^2 L_z}{2\pi} \leq \frac{3L_r^2}{4L_z^2} \tag{8}$$

$$\frac{2nL_z^3}{3\pi} \leq 1 \tag{9}$$

Using $n = 5.86 \cdot 10^{22}$ cm^{-3} and $L_z = 4.1$ Å in Eq. (9) we find $0.86 \leq 1$, thereby confirming that only $n_z = 1$ is filled. The energy of the highest occupied single particle level in the film of this thickness is

$$\varepsilon(n_x, n_y, 1) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L_r}\right)^2 (n_x^2 + n_y^2) + \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2 1^2 \tag{10}$$

$$\varepsilon(n_x, n_y, 1) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L_r}\right)^2 \frac{nL_r^2 L_z}{2\pi} + \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2 \tag{11}$$

Thus the Fermi energy, measured from the lowest energy level $(0,0,1)$, (or "bottom of the band" in general solid state terminology—note that we can always shift the reference energy level by a constant) is

$$\varepsilon_F = \varepsilon(n_x, n_y, 1) - \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2 = \frac{\hbar^2}{2m} 2\pi L_z n = 5.7 \text{ eV}. \tag{12}$$

In contrast to this result, the Fermi energy of the bulk metal would be

$$\varepsilon_F^{\text{box}} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = 5.48\,\text{eV}. \tag{13}$$

Part (b) requires to repeat similar steps where one finds that $n_z = 3$ level fills (by guessing that $n_z = 4$ fills and finding that it would fill with negative number of electrons). If number of electrons with $n_z = 1$ is N_1 [see Eq. (7], with $n_z = 2$ is N_2, and with $n_z = 3$ is N_3 then the total number of electrons is

$$n L_r^2 L_z = N_1 + N_2 + N_3 \tag{14}$$

while the highest occupied state satisfies

$$\frac{\hbar^2}{2m}\left[\left(\frac{2\pi}{L_r}\right)^2 \frac{N_1}{2\pi} + \left(\frac{\pi}{L_z}\right)^2 1^2\right] = \frac{\hbar^2}{2m}\left[\left(\frac{2\pi}{L_r}\right)^2 \frac{N_2}{2\pi} + \left(\frac{\pi}{L_z}\right)^2 2^2\right] = \frac{\hbar^2}{2m}\left[\left(\frac{2\pi}{L_r}\right)^2 \frac{N_3}{2\pi} + \left(\frac{\pi}{L_z}\right)^2 3^2\right] \tag{15}$$

From these equations one can find N_1, N_2, and N_3 and thereby $\varepsilon_F = 5.88$ eV (determined by either of these three numbers).