Physics 112 Fall 2017
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Homework 7 Solutions

Problem 1, Kittel 6.3: Double Occupancy Statistics

(a) In this problem we're considering a new particle which can at most *doubly* occupy an orbital (as opposed to single occupancy for fermions or unlimited occupancy for bosons). The Gibbs sum for a single orbital is then

$$\zeta = \sum_{N=0}^{2} e^{(N\mu - N\epsilon)/\tau} = 1 + e^{(\mu-\epsilon)/\tau} + e^{(2\mu-2\epsilon)/\tau}.$$

The average occupancy is given by the weighted sum:

$$\begin{aligned}
\langle N \rangle &= \frac{1}{\zeta} \sum_{N=0}^{2} N \lambda^N e^{-N\epsilon/\tau} \\
&= \frac{1}{\zeta} \left(0 \cdot 1 + 1 \cdot \lambda e^{-\epsilon/\tau} + 2 \cdot \lambda^2 e^{-2\epsilon/\tau} \right) \\
&= \frac{\lambda e^{-\epsilon/\tau} + 2 \cdot \lambda^2 e^{-2\epsilon/\tau}}{1 + \lambda e^{-\epsilon/\tau} + \lambda^2 e^{-2\epsilon/\tau}}.
\end{aligned}$$

(b) This question is poorly phrased, but by "usual quantum mechanics" they mean ordinary fermions. We're asked to consider ordinary fermions occupying two degenerate orbitals. Notice that in part (a) there was *one* orbital that could be doubly occupied, whereas in part (b) there are *two* orbitals that each can be at most singly occupied. This gives rise to four total system states: one with $N = 0$, two with $N = 1$, and one with $N = 2$. Using the ASN formalism from Kittel, we have

$$\begin{aligned}
\zeta &= \sum_{N=0}^{2} \sum_{s_N} e^{\left(N\mu - \epsilon_{s_N}\right)/\tau} = \sum_{N=0}^{2} \sum_{\epsilon} g\left(\epsilon\right) e^{(N\mu-\epsilon)/\tau} \\
&= 1 + 2 \cdot \lambda e^{-\epsilon/\tau} + \lambda^2 e^{-2\epsilon/\tau} = \left(1 + \lambda e^{-\epsilon/\tau} \right)^2.
\end{aligned}$$

Notice that the Gibbs sum for a single orbital would be $\zeta_1 = 1 + \lambda e^{-\epsilon/\tau}$, and so we have for the two orbital system $\zeta_2 = (\zeta_1)^2$, just as we did for the partition function in the canonical ensemble. (By way of terminology, the setting of the Gibbs sum, in which the system is allowed to trade energy *and* particles with the reservoir, is known as the *Grand canonical ensemble*.)

We then have

$$\begin{aligned}
\langle N \rangle &= \frac{1}{\zeta} \left(0 \cdot 1 + 2 \cdot \lambda e^{-\epsilon/\tau} + 2 \cdot \lambda^2 e^{-2\epsilon/\tau} \right) \\
&= \frac{2 \cdot \lambda e^{-\epsilon/\tau} + 2 \cdot \lambda^2 e^{-2\epsilon/\tau}}{1 + 2 \cdot \lambda e^{-\epsilon/\tau} + \lambda^2 e^{-2\epsilon/\tau}} \\
&= \frac{2}{e^{(\epsilon-\mu)/\tau} + 1}
\end{aligned}$$

which is just twice the Fermi-Dirac distribution, which gives the occupancy of one of the orbitals.

Problem 2, Kittel 6.4: Energy of Gas of Extreme Relativistic Particles

For a particle in a box we have

$$k_x = n_x \frac{\pi}{L} \implies p_x = n_x \frac{\hbar\pi}{L}$$

and so

$$E = |p|c = \sqrt{n_x^2 + n_y^2 + n_z^2}\,\frac{\pi}{L}\hbar c = n\frac{\pi}{L}\hbar c$$

where $n \equiv \sqrt{n_x^2 + n_y^2 + n_z^2}$. So the partition function for a single particle is:

$$Z_1 = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-|p|c/\tau} = \frac{1}{8}\int_0^\infty 4\pi n^2 dn\, e^{-\frac{\hbar c}{L\tau}n}.$$

Let $x = \frac{\hbar c}{L\tau}n$. Then

$$Z_1 = V\frac{4\pi\tau^3}{(2\pi\hbar)^3 c^3}\int_0^\infty dx\, x^2 e^{-x} \sim \tau^3$$

and so

$$U = \tau^2 \frac{\partial}{\partial \tau}\ln Z_1 = 3\tau^2 \frac{\partial}{\partial \tau}\ln \tau = 3\tau.$$

Problem 3: The Relation Between Pressure and Energy Density Revisited

(a) <u>Kittel 6.7</u>
Since the system is in thermal contact with a heat reservoir we are to assume that τ is constant. This prevents us from using Kittel's equation (25) from chapter 3,

$$p = -\frac{\partial \epsilon_s}{\partial V}$$

since that derivative is taken at constant entropy, as discussed below that equation. We may proceed, however, by using the relationship $p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N}$. The free energy is given by the partition function:

$$F = -\tau \ln Z = -\tau \ln\left(\sum_n e^{-\epsilon_n/\tau}\right),$$

$$\Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = \frac{\tau}{Z}\frac{\partial Z}{\partial V} = -\frac{1}{Z}\sum_n \frac{\partial \epsilon_n}{\partial V} e^{-\epsilon_n/\tau}.$$

(b) We know for a particle in a box with sides of length L the energy is given by

$$\epsilon_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{\hbar^2 \pi^2 n^2}{2m} V^{-2/3}.$$

The desired relation then follows by taking a derivative with respect to V:

$$\frac{\partial \epsilon_n}{\partial V} = \frac{\partial}{\partial V}\left(\frac{\hbar^2 \pi^2 n^2}{2m}V^{-2/3}\right) = -\frac{2}{3}\frac{\epsilon_n}{V}$$

(c) Now we just need to plug (a) into (b):

$$
\begin{aligned}
p &= -\frac{1}{Z}\sum_n \frac{\partial \epsilon_n}{\partial V} e^{-\epsilon_n/\tau} = -\frac{1}{Z}\sum_n \left(-\frac{2}{3}\right)\frac{\epsilon_n}{V} e^{-\epsilon_n/\tau} \\
&= \frac{2}{3V}\frac{\sum_n \epsilon_n e^{-\epsilon_n/\tau}}{Z} = \frac{2U}{3V}
\end{aligned}
$$

because $U = \frac{1}{Z}\sum_n \epsilon_n e^{-\epsilon_n/\tau}$.

(d) To find the pressure of a Fermi gas, we need an expression for the total energy using the fact that we're given the number density of electrons. We have the energy in terms of the Fermi energy $U = \frac{3}{5}N\epsilon_F$ and the Fermi energy is determined by the number density: $\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$. We can then find the pressure using the expression above:

$$
\begin{aligned}
p &= \frac{2U}{3V} = \frac{2N\epsilon_F}{5V} = \frac{2n\epsilon_F}{5} \\
&= \frac{2}{5}\cdot\left(8\cdot 10^{28}\frac{1}{\text{m}^3}\right)\left(7\cdot 1.6\cdot 10^{-19}\text{ J}\right)\left(10^{-5}\frac{\text{Atm}}{\text{Pascal}}\right) \\
&= 3.6\cdot 10^5 \text{ Atm}.
\end{aligned}
$$

Problem 4, Kittel 6.9 : Gas of atoms with internal Degrees of Freedom

Because we have two internal states separated by an energy difference Δ we can write down the internal partition function:

$$Z_{\text{int}} = 1 + e^{-\Delta/\tau}$$

As always, adding a constant to these energies does not affect any physical quantities, so we can set the energy of the lower energy state to zero.

(a) To find the chemical potential we can use the result we found in lecture (and the book):

$$\mu = \tau\left[\ln(n/n_Q) - \ln Z_{\text{int}}\right] = \tau\left[\ln(n/n_Q) - \ln\left(1 + e^{-\Delta/\tau}\right)\right]$$

(b) Similarly, the free energy is:

$$F = N\tau\left[\ln(n/n_Q) - 1\right] - N\tau\ln Z_{\text{int}} = N\tau\left[\ln(n/n_Q) - 1\right] - N\tau\ln\left(1 + e^{-\Delta/\tau}\right)$$

(c) The total entropy is the ideal gas entropy plus the internal entropy:

$$\sigma = -\frac{\partial F}{\partial \tau}\Big|_{V,N} = N\left[\ln(n_Q/n) + \frac{5}{2}\right] + N\ln\left(1 + e^{-\Delta/\tau}\right) + \frac{N\Delta}{\tau}\frac{1}{e^{\Delta/\tau}+1}$$

(d) We can calculate the pressure from the free energy:

$$p = -\frac{\partial F}{\partial V}\Big|_{\tau,N} = \frac{N\tau}{V}$$

(e) To find the heat capacity at constant pressure we need to use the relation:

$$C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p$$

We know the contribution from an ideal gas is $C_p^{IG} = \frac{5}{2}N$, so we just need to find the contribution from the internal degree of freedom. The energy from the internal degree of freedom is given by:

$$
\begin{aligned}
U_{\text{int}} &= F_{\text{int}} - \sigma_{\text{int}}\tau \\
&= -N\tau \ln\left(1 + e^{-\triangle/\tau}\right) + N\tau\left[\ln\left(1 + e^{-\triangle/\tau}\right) + \frac{\triangle}{\tau(e^{\triangle/\tau} + 1)}\right] \\
&= \frac{N\triangle}{e^{\triangle/\tau} + 1}.
\end{aligned}
$$

The internal degree of freedom doesn't depend of volume, so the second term in C_p won't contribute, so the heat capacity contribution from the internal degrees of freedom is

$$
C_p(\text{int}) = \tau\frac{\partial\sigma}{\partial\tau}\Big|_p = \frac{\partial U}{\partial\tau}\Big|_p + p\frac{\partial V}{\partial\tau}\Big|_p.
$$

Thus the total heat capacity at constant pressure of the gas is

$$
C_p = \frac{5}{2}N + \frac{N\triangle^2}{\tau^2}\frac{e^{\triangle/\tau}}{(e^{\triangle/\tau} + 1)^2}.
$$

Problem 5, Kittel 6.12 : Ideal Gas in Two Dimensions

Two dimensional systems, in particular 2D electron gases, can be created experimentally and have resulted in the discovery of some very interesting phenomena (including, for example, the fractional Quantum Hall effect where charges that are fractions of the electron charge appear) and several Nobel Prizes, so don't think of this problem as purely a mathematical exercise.

(a) Our strategy for finding μ will be to compute the single-particle partition function Z_1, use this to find the free energy, and then use $\mu \equiv \left(\frac{\partial F}{\partial N}\right)\big|_{\tau,V}$. Using the energies of a particle in a 2D box $\epsilon_n = \frac{\pi^2\hbar^2}{2mL^2}n^2$ with $n^2 = n_x^2 + n_y^2$, we have

$$
\begin{aligned}
Z_1 &= \sum_n e^{-\epsilon_n/\tau} = \frac{2\pi}{4}\int_0^\infty n\,dn\,e^{-\frac{\pi^2\hbar^2}{2mL^2\tau}n^2} \\
&= \frac{\pi}{2}\left(\frac{mL^2\tau}{\pi^2\hbar^2}\right)\int_0^\infty dx\,e^{-x} \\
&= \frac{mL^2\tau}{2\pi^2\hbar^2} \equiv An_Q^{2D} \quad\quad\quad\quad (1)
\end{aligned}
$$

where we've defined the two dimensional quantum concentration

$$
n_Q^{2D} \equiv \frac{m\tau}{2\pi\hbar^2}.
$$

Notice that (**??**) follows the general form of the partition function in 3D. The N-particle partition function is then just $Z_N = Z_1^N/N!$ and so the free energy is

$$
\begin{aligned}
F &= -\tau\ln\left(\frac{Z_1^N}{N!}\right) = -\tau\left[N\ln Z_1 - N\ln N + N\right] \\
&= N\tau\left[\ln\left(N/Z_1\right) - 1\right]. \quad\quad\quad\quad (2)
\end{aligned}
$$

We then have

$$
\begin{aligned}
\mu &= \left. \left(\frac{\partial F}{\partial N} \right) \right|_{\tau, V} \\
&= \tau \left[\ln(N/Z_1) - 1 \right] + \tau \\
&= \tau \ln \left(n/n_Q^{2D} \right).
\end{aligned}
$$

(b) We can then directly compute

$$
U = \tau^2 \frac{\partial \ln Z_N}{\partial \tau} = N\tau^2 \frac{\partial \ln Z_1}{\partial \tau} = N\tau. \tag{3}
$$

Of course we should have been able to write this result down right away from the equipartition theorem. In 2D, each particle has two degrees of freedom, so the energy per particle in the classical limit of an ideal gas should be $U/N = 2 \cdot \frac{1}{2}\tau = \tau N$.

(c) Using **(??)** and **(??)** we calculate the entropy as $\sigma = (U - F)/\tau = N \left[\ln \left(\frac{n_Q^{2D}}{n} \right) + 2 \right]$, which is totally analogous to the usual Sackur-Tetrode equation, with the $+ 5/2$ becoming a $+2$.

Problem 6: Chemical Equilibrium Between Electrons and Holes

Before we start this problem, it's important to make sure we understand the basics of the band structure of semiconductors (and insulators). Our model of a metal as a free Fermi gas with a continuum of energy levels ignored the interaction of the electrons with the positive nuclei in a solid. The periodic potential from the positive ions creates regions of energy of the Fermi gas that have no states, so the continuum of energy levels in the fermi gas is divided into bands of continuous states which are separated by energy gaps with no electron states. A metal has a partially filled band, so there are empty electron states infinitesimally close to the Fermi level. The Fermi level in insulators and semiconductors exactly coincides with the top of a band (called the valence band), so the nearest empty states (in the conduction band) are separated by the energy gap from the Fermi level.

In a semiconductor at finite temperatures a few electrons from the valence band will be excited into the conduction band, leaving empty states in the valence band. These empty states act like positively charged particles called 'holes'. When an electron falls back from the conduction band into the valence band, we consider this as an electron and hole annihilating, and the energy of the particles is carried away by phonons (this is analogous to an electron and positron annihilating to create photons).

In this problem we want to consider this process of conduction electrons falling back into the valence band, so all chemical potentials and number densities of electrons refer to *conduction* electrons. We're not physically destroying an electron, just destroying a conduction electron by putting it back in the valence band.

(a) The equation $\mu_e + \mu_h = 0$ refers to the chemical potential of the *conduction* electrons and the holes respectively. These are two separate systems whose particle numbers are related, but instead of having $N_e + N_h = $ constant, as is usually the case, we have $N_e = N_h$ because exciting an electron into the conduction band creates a hole in the valence band. This is why our equilibrium condition is $\mu_e + \mu_h = 0$ instead of $\mu_e = \mu_h$.

Furthermore, we're assuming that the concentration of conduction electrons and holes is low, so that we may model these as ideal gases rather than degenerate Fermi gases. We know that exciting an electron into the conduction band will cost E_g of energy, so this energy gap acts as an external chemical potential for the electron and hence

$$
\mu_e = \tau \ln \left(\frac{n_e}{2n_{Q_e}} \right) + E_g, \tag{4}
$$

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where the factor of two in the denominator comes from the two-fold spin degeneracy. Since $n_e = n_h$, the hole chemical potential is simply

$$\mu_h = \tau \ln \left(\frac{n_h}{2n_{Q_h}} \right) = \tau \ln \left(\frac{n_e}{2n_{Q_h}} \right).$$

Note that the quantum concentrations for the holes and conduction electrons are different since they have different effective masses.

We can now compute:

$$
\begin{aligned}
0 &= \mu_e + \mu_h \\
&= E_g + \tau \ln \left(\frac{n_e}{2n_{Q_e}} \right) + \tau \ln \left(\frac{n_h}{2n_{Q_h}} \right) \\
\implies n_e \cdot n_h &= 4n_{Q_e} \cdot n_{Q_h} e^{-E_g/\tau}. && (5) \\
\implies n_e &= 2 \left(\frac{\tau \sqrt{m_e \cdot m_h}}{2\pi\hbar^2} \right)^{3/2} e^{-E_g/2\tau} && (6)
\end{aligned}
$$

since $n_e \cdot n_h = n_e^2$.

(b) Now we can plug **(??)** back into **(??)** to get

$$
\begin{aligned}
\mu_e &= E_g + \tau \ln \left(\frac{2\sqrt{n_{Q_e} n_{Q_h}} e^{-E_g/2\tau}}{2n_{Q_e}} \right) \\
&= E_g + \tau \ln \left(\sqrt{\frac{n_{Q_h}}{n_{Q_e}}} e^{-E_g/2\tau} \right) \\
&= \frac{E_g}{2} + \frac{3\tau}{4} \ln \left(\frac{m_h}{m_e} \right).
\end{aligned}
$$

(c) If a semiconductor is doped with a small amount of another element, these impurities can create donor energy levels that put a small number of extra electrons into the conduction band. This gives the relationship

$$n_e' = n_h' + n_D. \tag{7}$$

Equation **(??)** also still holds for n_e' and n_h', which gives

$$n_e' \cdot n_h' = 4n_{Q_e} \cdot n_{Q_h} e^{-E_g/\tau} = n_e^2$$

where n_e is the old (pre-doping) electron density. Combining these last two equations gives

$$
\begin{aligned}
n_e' \cdot n_h' &= n_e^2 \\
\implies n_e' \cdot (n_e' - n_D) - n_e^2 &= 0, \\
\implies n_e' &= \frac{n_D}{2} + \sqrt{\frac{n_D^2}{4} + n_e^2}.
\end{aligned}
$$

Unsurprisingly, this tells us that doping a semiconductor will increase the density of conduction electrons.