Solution of homework # 11

Exercise 2 – The Fermi-Dirac distribution function

1. The function $n(\varepsilon) = \frac{1}{1+e^{(\varepsilon-\mu)/k_\mathrm{B}T}}$ is represented in Fig. 1, for $\mu = 2\,\mathrm{eV}$ and $T = 0\,\mathrm{K}$, in green and $T = 1200\,\mathrm{K}$, in blue. It represents the probability that a state with energy ε will be occupied by an electron. The complementary function $1 - n(\varepsilon)$, dashed blue line, represents the probability that a state will be empty, or, equivalently, occupied by a hole.

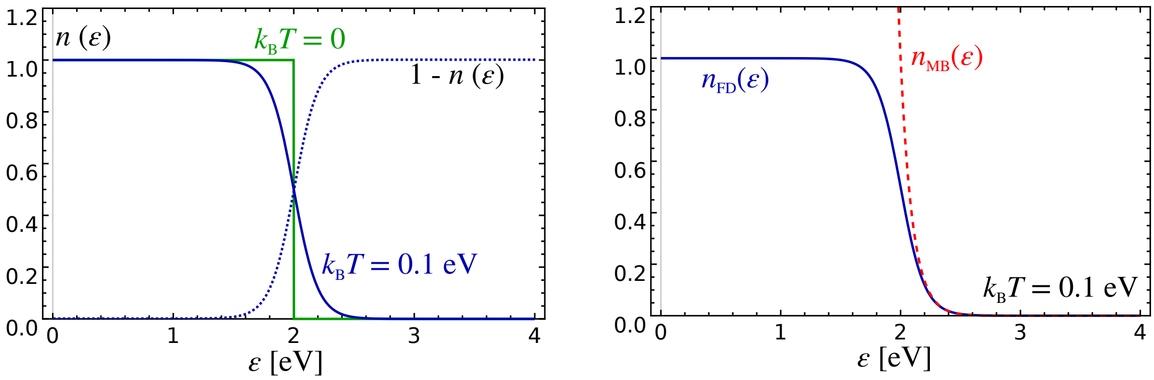

Figure 1: *Left: Fermi-Dirac distribution for two values of temperature. Right: comparison between Fermi-Dirac distribution and its classical limit, the Maxwell-Boltzmann distribution*

A state with energy equal to the chemical potential will have a probability $n(\mu) = \frac{1}{2}$ of being occupied, which does not depend on T. The probability that a state at $\varepsilon = 2\mu$ will be empty is $1 - n(2\mu) = 1 - \frac{1}{1+e^{\mu/k_\mathrm{B}T}} = \frac{1}{1+e^{-\mu/k_\mathrm{B}T}}$. With the values used to plot the figure above, a state at $4\,\mathrm{eV}$ will have probability one of being empty at $T = 0\,\mathrm{K}$, and probability $\approx \frac{1}{1+e^{-20}} \approx 0.999999996$ at $T = 1200\,\mathrm{K}$. Still, basically, one: one needs extremely high temperatures to thermally populate high-energy states.

2. The assumption is that $n(\varepsilon_\mathrm{v}) = 1 - n(\varepsilon_\mathrm{c})$, that is:

$$\frac{1}{1+e^{(\varepsilon_\mathrm{v}-\mu)/k_\mathrm{B}T}} \stackrel{!}{=} 1 - \frac{1}{1+e^{(\varepsilon_\mathrm{c}-\mu)/k_\mathrm{B}T}} = \frac{1}{1+e^{(\mu-\varepsilon_\mathrm{c})/k_\mathrm{B}T}} \implies \varepsilon_\mathrm{v} - \mu = \mu - \varepsilon_\mathrm{c} \implies \mu = \frac{\varepsilon_\mathrm{v}+\varepsilon_\mathrm{c}}{2}.$$

Using the fact that the gap is defined as $E_g = \varepsilon_\mathrm{c} - \varepsilon_\mathrm{v}$, we obtain:

$$\mu = \varepsilon_\mathrm{v} + \frac{E_g}{2},$$

namely the chemical potential is in the middle of the gap. Plugging in the values given in the text we obtain $\mu = \varepsilon_\mathrm{v} + \frac{E_g}{2} = 12\,\mathrm{eV} + \frac{1.1\,\mathrm{eV}}{2} = 12.55\,\mathrm{eV}$.

3. The Maxwell-Boltzmann distribution is always larger than the Fermi-Dirac one. Above a certain energy $\bar{\varepsilon}$, the two will differ by less than 1/100 (see Fig. 1). The equation to be solved is:

$$\left(e^{-(\varepsilon-\mu)/k_\mathrm{B}T} - \frac{1}{1+e^{(\varepsilon-\mu)/k_\mathrm{B}T}} \right)\Bigg|_{\varepsilon=\bar{\varepsilon}} = \frac{1}{100}.$$

Let us call $x \equiv e^{(\bar{\varepsilon}-\mu)/k_{\mathrm{B}}T} > 0$, and the above equation then reads:

$$\frac{1}{x} - \frac{1}{1+x} = \frac{1}{100} \quad \Longrightarrow x^2 + x - 100 = 0 \quad \Longrightarrow \quad x = 9.51 \approx 10.$$

Only the positive solution is kept, since x is an exponential. Substituting the solution back, we get $e^{(\bar{\varepsilon}-\mu)/k_{\mathrm{B}}T} = 10$ and hence $\bar{\varepsilon} = \mu + k_{\mathrm{B}}T \ln 10 \approx \mu + 2.3k_{\mathrm{B}}T$, which is most of the times very close to μ itself. In the Fig 1, it can be seen that at an energy 0.2 eV higher than μ we can approximate the Fermi-Dirac with the Maxwell-Boltzmann distribution, committing an error smaller than 1%.

Exercise 2 – Effective masses and band gap

1. As written in the homework, the effective mass is given by the relation $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}$: the more peaked the band structure $E(k)$ is, the lighter the mass will be; and the flatter the band structure, the heavier the mass. Therefore the upper band (the green one in the cartoon) is the heavy valence band, while the lower one (the blue one) is the light valence band. In the band structure plot, these are the first and second valence bands at the Γ point (counting valence bands from the top to the bottom), whose highest energy ε_{v} is zero (by convention, this is most often the case in band structure representations, as there is always the freedom to set the zero of the energy anywhere).

2. The two valence bands yield the two densities of states:

$$g_{hh}(\varepsilon) = \frac{m_{hh}^{3/2}}{\pi^2\hbar^3}\sqrt{2(\varepsilon_{\mathrm{v}} - \varepsilon)}, \qquad g_{lh}(\varepsilon) = \frac{m_{lh}^{3/2}}{\pi^2\hbar^3}\sqrt{2(\varepsilon_{\mathrm{v}} - \varepsilon)}.$$

The total density of states is simply the sum of the two:

$$g_{\mathrm{v}}(\varepsilon) = g_{hh}(\varepsilon) + g_{lh}(\varepsilon) = \frac{m_{hh}^{3/2} + m_{lh}^{3/2}}{\pi^2\hbar^3}\sqrt{2(\varepsilon_{\mathrm{v}} - \varepsilon)}.$$

By comparison with the density of states of a hypothetical single valence band with effective mass m_v, $g_{\mathrm{v}}(\varepsilon) = \frac{m_{\mathrm{v}}^{3/2}}{\pi^2\hbar^3}\sqrt{2(\varepsilon_{\mathrm{v}} - \varepsilon)}$, we see that the latter is given by

$$m_{\mathrm{v}} = (m_{hh}^{3/2} + m_{lh}^{3/2})^{2/3}.$$

For GaAs, we obtain the value $m_v = m(0.45^{3/2} + 0.082^{3/2})^{2/3} = 0.47m$.

3. The relation between energy and wavelength is the Planck-Einstein relation $E = \frac{hc}{\lambda}$. Therefore, if a photon has energy E, its wavelength is $\lambda = \frac{hc}{E}$, with $hc = 1.24\,\mathrm{eV}\cdot\mu\mathrm{m}$.

If a system displays an energy gap E_g, only photons with energies greater than E_g will be able to excite electrons from the valence to the conduction bands. While these electrons will be absorbed by the material, the others will be transmitted. Therefore, the material will be opaque to any wavelength shorter than $\frac{hc}{E_g}$ and transparent to larger wavelengths. Let us collect these wavelengths for the set of materials considered:

Considering that visible light falls into the range $400 - 700\,\mathrm{nm}$, the three semiconductors are opaque to any visible wavelength.

	E_g [eV]	hc/E_g [nm]
C (diamond)	5.50	225
GaN (LED)	3.44	360
GaP	2.26	549
Na	0.00	∞
GaAs	1.42	873
Si	1.12	1107
Ge	0.67	1851

GaP adsorbs all wavelengths shorter than 550 nm: in particular, it absorbs the green, the blue and the violet. On the contrary, yellow, orange and red wavelengths are not energetic enough to be absorbed, and they are transmitted. That is why GaP looks orange.

GaN is a wide-gap semiconductor (almost an insulator), whose gap is too large to allow photons of visible wavelengths to be absorbed. Therefore, it is transparent, and it is indeed used in LEDs devices. Note, however, that for butterflies who see in the ultraviolet like the *Sara Longwing* butterfly (whose visual range starts at 310 nm), GaN would look opaque too.

Finally, diamond is clearly transparent, both for humans and for butterflies.