

Mandatory assignment FYS3400 III

Candidate n. 110

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Exercise 1

The honeycomb lattice is a special case of the hexagonal lattice with a two-atom basis. Especially the centers of the hexagons of a honeycomb form a hexagonal lattice. As a consequence, we can write the hexagonal lattice basis:

$$a_1 = \frac{3a}{2}e_x + \frac{\sqrt{3}a}{2}e_y \quad a_2 = \frac{3a}{2}e_x - \frac{\sqrt{3}a}{2}e_y$$

with $a = 1.42\text{\AA}$.

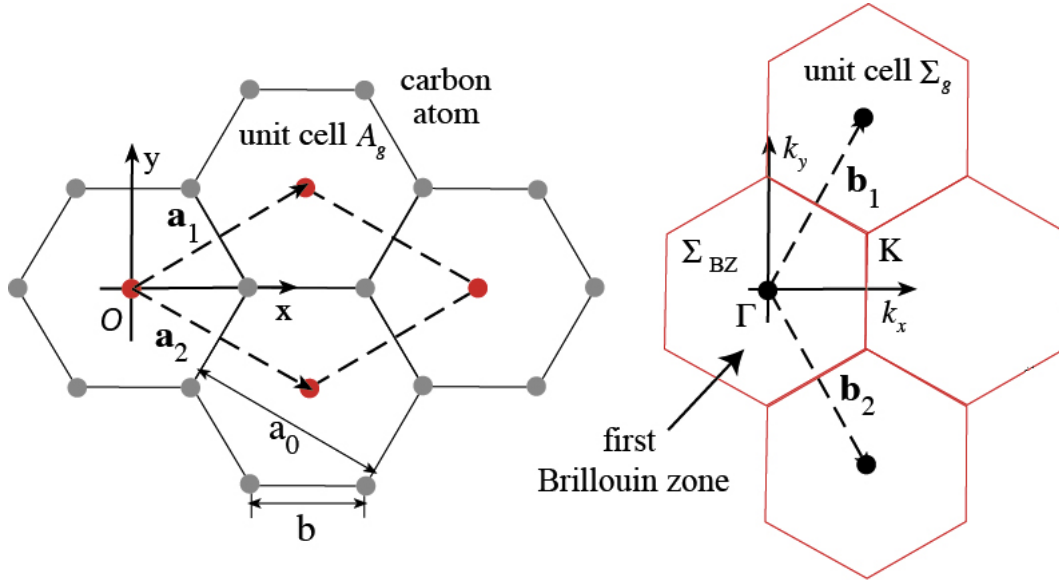


Figure 1: On the left the figure shows a special case of the hexagonal lattice with a two-atom basis to representing the graphene geometry. On the right side the figure shows the reciprocal space, and the brillouin zone

In order to study the energy gap and the effective mass we can move to the reciprocal space through the following coordinate change:

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

This yields to a new set of basis:

$$b_1 = \frac{2\pi}{a} \left(\frac{1}{3}\hat{k}_x + \frac{1}{\sqrt{3}}\hat{k}_y \right) \quad b_2 = \frac{2\pi}{a} \left(\frac{1}{3}\hat{k}_x - \frac{1}{\sqrt{3}}\hat{k}_y \right)$$

The energy bands behaviour of the graphene sheet is given by:

$$E(k) = \pm t \left[1 + 4\cos\left(\frac{\sqrt{3}ak_y}{2}\right)\cos\left(\frac{3ak_x}{2}\right) + 4\cos^2\left(\frac{\sqrt{3}ak_y}{2}\right) \right]^{\frac{1}{2}} \quad (1)$$

The exercise asks to plot the energy bands along specific directions: $[0,1]$, $[1,0]$, $[1,1]$, i.e along $K = 0b_1 + 1b_2$, $K = 1b_1 + 0b_2$, $K = 1b_1 + 1b_2$. To do that we can substitute K and its components (k_x and k_y) into the given energy formula (1). Thus, we plot the energy bands along the requested directions. The plots are shown in figure 2. Additionally, it is possible to see the general behavior of the lower energy band with an heatmap, as it is shown in figure 3.

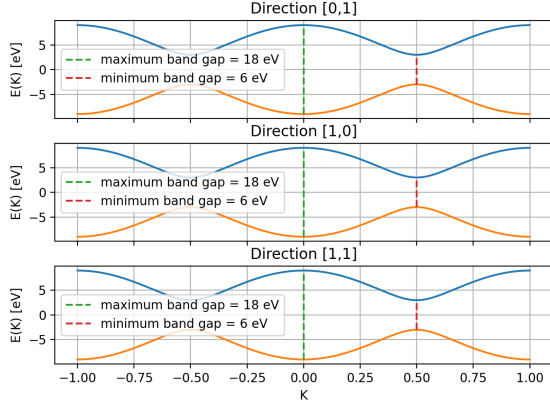


Figure 2: Energy bands along 3 different directions. The k axis has units of $\frac{2\pi}{a}$

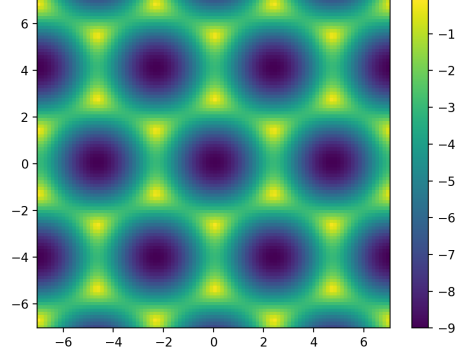


Figure 3: This is the energy heatmap of the lower energy band. the color bar represent the eV. From the figure we can clearly see the honeycomb composition.

Effective mass

Using the traditional semi-classical approach by associating particles with wave-packets, we can link the particle velocity with the group velocity of a wave-packet and the particle momentum with the crystal momentum $\vec{p} = \hbar \vec{k}$. Then,

$$\vec{v}_g = \nabla_{\vec{k}} \omega(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} E(\vec{k})$$

With this in mind, the effective mass appears as a proportionality factor between the particle momentum and the group velocity of the wave-packet:

$$\vec{p} = \hbar \vec{k} \sim m^* \vec{v}_g$$

It should be noted that the effective mass can change value depending on the direction where the wave-packets is moving. Hence, to derive a scalar expression for the mass along a direction we can consider the projection along the direction vector, in other words considering the directional derivative. In that case we obtain¹:

$$m_{\vec{d}}^* = \hbar^2 \frac{\vec{d} \cdot \vec{k}}{\vec{d} \cdot \nabla_{\vec{k}} E(\vec{k})} \quad (2)$$

where \vec{d} indicates the direction where we want to find the effective mass while the wave-packet is moving along \vec{k} . In other words, if we apply a force along \vec{d} while the electron/hole propagates along \vec{k} , then we find that the electron/hole has effective mass described by equation (2).

Note that this expression is more general rather than $m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$, that it is a good approximation only around a stationary point. We can now evaluate the gradient and plot the effective mass as a function of the direction.

We calculated the effective mass in the Gamma point getting: $m_{\Gamma} = +11.027 \left[\frac{\hbar^2}{(nm)^2 eV} \right] \approx 0.84 m_e$. Moreover, the Γ point corresponds to a stationary point in the energy band and the behaviour is almost parabolic around it. Hence, in this approximation we can also use the well known formula for the effective

$$m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1} \quad (3)$$

obtaining the same result of equation (2). On the other hand, we running into a different situation near the Dirac point (Edge of Brillouin zone). We find that graphene has an infinite effective mass by the definition (2) and (3), this is because the behaviour of the energy around these points is linear in k and it gives a divergence, as we can see in figure 5 and 6. As well as that we have also used a non-relativistic definition of mass.

¹For the sake of completeness, here we put the gradient's components:

$$\frac{\partial E(\vec{k})}{\partial k_x} = \pm \frac{t^2}{E(\vec{k})} \left(-3a \cos\left(\frac{\sqrt{3}a}{2} k_y\right) \sin\left(\frac{3a}{2} k_x\right) \right) \quad \frac{\partial E(\vec{k})}{\partial k_y} = \pm \frac{t^2}{E(\vec{k})} \left(-\sqrt{3}a \sin\left(\frac{\sqrt{3}a}{2} k_y\right) \cos\left(\frac{3a}{2} k_x\right) - \sqrt{3} \sin(\sqrt{3}a k_y) \right)$$

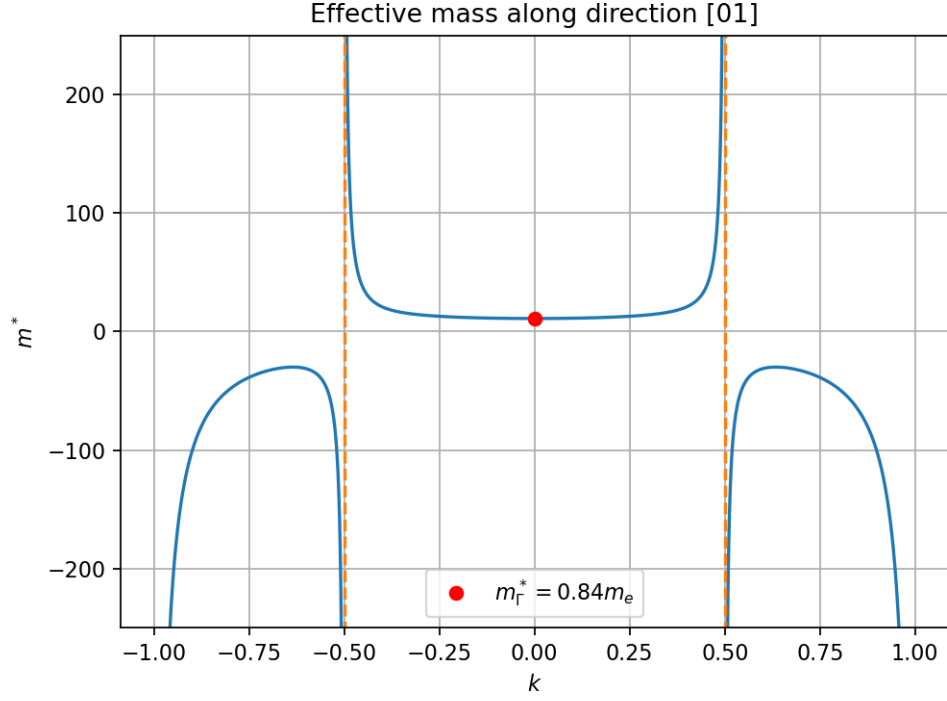


Figure 4: This figure shows the effective mass along the direction $[0,1]$, i.e $\vec{d} = \frac{1}{3}\hat{k}_x + \frac{1}{\sqrt{3}}\hat{k}_y$, doing the limit $\lim_{\vec{k} \rightarrow \vec{0}}$ we get $m_{\Gamma}^* = +11.027[\frac{\hbar^2}{(nm)^2 eV}] = 0.84m_e$.

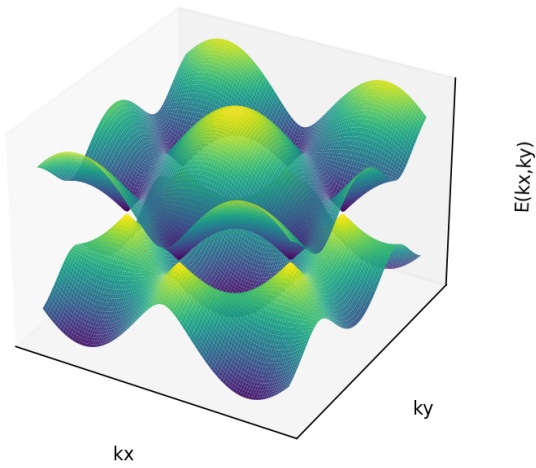


Figure 5: 3D plot of the energy bands of graphene sheet according to equation 1

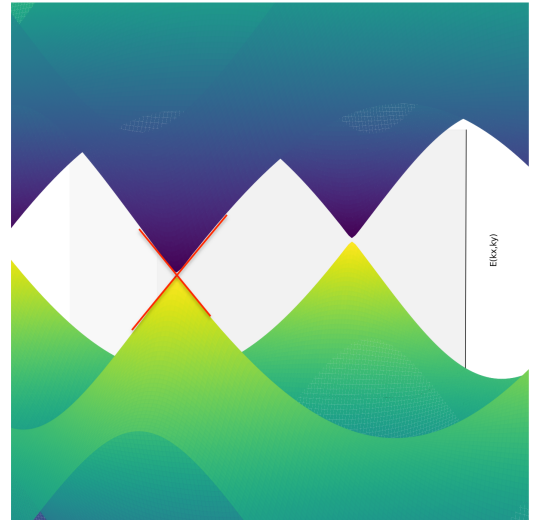


Figure 6: This figure is a zoom in of figure 5 around a dirac point. In red is enlightened the linear behaviour around this points, which gives a divergence in the effective mass

Exercise 2

Before studying the extrinsic behaviour, it is necessary describe the intrinsic one. We know that the carrier concentration in the conduction level for an intrinsic semiconductor is given by:

$$\begin{aligned} n &= \int_{E_c}^{+\infty} Dos(\epsilon) f(\epsilon) d\epsilon \\ &= 2 \left(\frac{m_e^* k_b T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{E_{F_i} - E_c}{k_b T}} = N_c e^{\frac{E_{F_i} - E_c}{k_b T}} \end{aligned} \quad (4)$$

where $Dos(\epsilon)$ is the density of states and $f(\epsilon)$ is the Fermi-Dirac distribution. The N_c term is temperature dependent called the effective density of states of the conduction band; and last but not least E_{F_i} is the intrinsic Fermi energy. On the other hand the hole concentration (lack of electron in valence band by the excitation of an electron) is given similarly by:

$$\begin{aligned} p &= \int_{-\infty}^{E_v} Dos(\epsilon) (1 - f(\epsilon)) d\epsilon \\ &= 2 \left(\frac{m_h^* k_b T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{E_v - E_{F_i}}{k_b T}} = N_v e^{\frac{E_v - E_{F_i}}{k_b T}} \end{aligned} \quad (5)$$

where N_v is a temperature dependent constant called the effective density of states of the valence band. Moreover, if we multiply equation 4 and equation 5 we obtain:

$$np = 4 \left(\frac{k_b T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{\frac{3}{2}} e^{-\frac{E_g}{k_b T}} = n_i^2$$

This quantity does not depend on the Fermi energy E_F , which is a quantity that changes when a semiconductor is doped. Hence, this relationship is true also in the case of a doped semiconductor. Furthermore, in a intrinsic semiconductor $n = p$ and we have $n = p = n_i$. This is because the product of the electron and hole concentration is a constant, not depending on the impurity concentration at given temperature. The introduction of a small proportion of a suitable impurity to increase n, say, must decrease p.

The property $n = p$ in an intrinsic semiconductor gives us the possibility to estimate the so called intrinsic Fermi energy, equalling equation 4 and equation 5:

$$\begin{aligned} n &= p \\ N_c e^{\frac{E_{F_i} - E_c}{k_b T}} &= N_v e^{\frac{E_v - E_{F_i}}{k_b T}} \\ E_{F_i} &= \frac{E_c + E_v}{2} + \frac{3}{4} k_b T \ln \left(\frac{m_h^*}{m_e^*} \right) \end{aligned}$$

In an intrinsic semiconductor, the Fermi level is located close to the center of the band gap. Note that this quantity depends only on the band gap and on the electron and hole effective masses. In an extrinsic semiconductor, the general behaviour is slightly different, with the dopants fully ionized, there is an imbalance in the electron and hole concentration. This in turn is reflected in the Fermi level position being shifted from the center of the band gap towards either the conduction band for an n-type or valence band for an p-type. We are dealing with a P-doped silicon, i.e n-type doping, since phosphorus is an element of the fifth group, and the Fermi energy is shifted towards the conduction band. The carrier concentration is calculated as in equation 4, but this time we have a different Fermi energy, depending on the donor concentration. For the sake of clarity, we can write the carrier concentration expression using E_{F_i} and n_i , since these are intrinsic parameters of the semiconductor and they don't depend on the donor.

$$n = N_c e^{\frac{E_{F_i} - E_c}{k_b T}} = N_c e^{\frac{E_{F_i} - E_c}{k_b T}} e^{\frac{E_{F_i} - E_i}{k_b T}} = n_i e^{\frac{E_{F_i} - E_i}{k_b T}} \quad (6)$$

We shifted the problem on the Fermi energy behaviour relative to the intrinsic case. Now we have to determine this new Fermi energy. To do that we start from the charge neutrality (the semiconductor must be neutral overall):

$$p + N_d^+ = n \quad (7)$$

Where N_d^+ indicates the concentration of the positive charge of the donor (the lack of electrons in the donor band, or indirectly how many electrons have been excited to the conduction band ²):

$$N_d^+ = N_d (1 - f(E_D)) = N_d \left(1 - \frac{1}{1 + g^{-1} e^{\frac{(E_D - E_f)}{k_b T}}} \right) = \frac{N_d}{1 + g e^{\frac{(E_F - E_D)}{k_b T}}}$$

²Pay attention, the lack of electrons in the donor band doesn't mean that we have holes in the donor level, because these positive charge are localised and cannot move away from the impurity

Where g is a factor that take into account the degeneracy of the level. We use $g = 2$ to account the spin degeneracy. Now that we have all the ingredients the neutrality equations becomes:

$$n_i e^{\frac{E_{F_i} - E_F}{k_b T}} + \frac{N_d}{1 + 2e^{\frac{E_F - E_D}{k_b T}}} = n_i e^{\frac{E_F - E_{F_i}}{k_b T}} \quad (8)$$

An analytic solutions can only be found in special limiting cases and we later proceed to discuss some of these. Hence, we proceeded to solve this equation numerically and find the the Fermi energy for every temperature. First, to solve (8) we need to set some parameters, this parameters depend on the material and on the donor, since we are dealing with silicon we have:

$$m_e^* = 1.08m_e \quad m_h^* = 0.56m_e \quad E_v = 0eV \quad E_c = 1.1eV \quad E_D = 1.055eV \quad N_d = 10^{17} \frac{P_{atoms}}{cm^3}$$

where m_e is the mass of the electron. According to this parameters we plotted the Fermi energy behaviour over temperature, as it is shown in figure 7.

We can see that an increase in temperature makes the Fermi energy approaching the intrinsic level E_i ; moreover, stronger doping means higher Fermi energy, where at low temperature this is shifted forward to the conduction band. In the light of the above, once we obtained the Fermi energy we can compute the electron carrier concentration in a doped semiconductor using equation (6). The plot of the carrier concentration in the conduction band is shown in figure 8

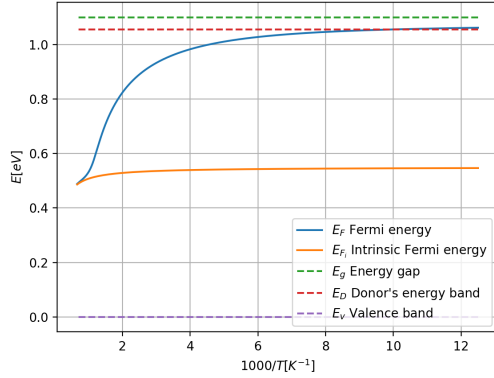


Figure 7: This figure shows the trend of the Fermi energy with the doping relative to the intrinsic Fermi energy over the temperature domain.

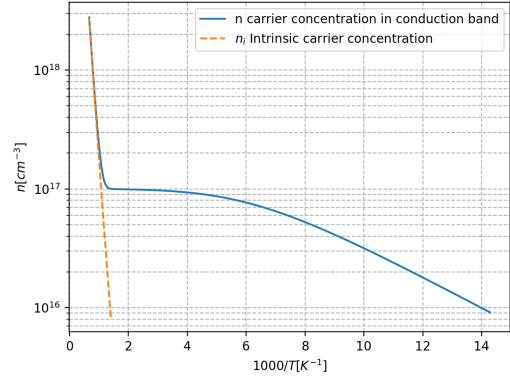


Figure 8: This figure shows the carrier concentration over the temperature domain.

Low temperature (freeze-out region)

At absolute zero there are no ionized carriers. Valence band is full and the donor level is full and conduction band is empty. As temperature is increased, electrons are excited from the valence band and the donor level to the conduction band. But since the valence band ionization energy is of the order of eV , at low temperature the number of electrons excited from it are negligible compared to the electrons from the donor level. This approximation applies on the charge neutrality as follow:

$$N_d^+ \approx n$$

This equation is simpler and it can be solved analytically making an approximation on the Fermi-Dirac distribution, which tend to the Boltzmann distribution in the limit of low particle density (small N_d^+ , hence low Temperature):

$$N_d^+ \approx n$$

$$\frac{N_d}{2} e^{\frac{E_D - E_F}{k_b T}} = N_c e^{-\frac{E_c - E_F}{k_b T}}$$

yielding to:

$$E_F = \frac{E_c + E_D}{2} + \frac{k_b T}{2} \ln \left(\frac{N_d}{2N_c} \right) \quad (9)$$

This means that the higher the donor concentration, the more E_F approaches the conduction band. Now, thanks to this, we can compute the negative free carrier concentration in low temperature regime using the general equation (4) and (9):

$$n = N_c e^{\frac{E_F - E_c}{k_b T}} = N_c \exp \left(\frac{\frac{E_c + E_D}{2} + \frac{k_b T}{2} \ln \left(\frac{N_d}{2N_c} \right) - E_c}{k_b T} \right) = \sqrt{\frac{N_d N_c}{2}} e^{-\frac{E_c - E_D}{2k_b T}}$$

We can see the good behaviour in this regime in figure 9. Consequently for low temperatures we expect that the concentration of holes is much lower than that of electrons (given mainly from the donor), and becomes very low when N_d becomes very large, in fact $p = \frac{n_i^2}{N_d^+} \ll N_d^+$. In conclusion at low enough temperature we have a range where carriers tend to freeze around impurities and the concentration is strongly dependent on temperature, in a so-called freeze-out range.

Medium temperatures (Saturation region) At medium temperatures the energy $k_b T$ is still not enough to promote an electron from the valence band to the conduction band, but all the electrons given by the donor have been promoted to the conduction band. Hence, we expect that the carrier concentration is flattened out at N_d , as it is shown in figure 9. Hence, there is a saturation range where the concentration is determined by doping and all the impurities are ionised: this is where usually lies the working range of the device.

High temperature (Intrinsic range) In the end, when we pass to high temperature regime we cannot ignore anymore the contributions from the intrinsic concentration n_i . If this is the case, in this temperature domain the energy is enough to promote an electron from the valence band to the conduction band. Now the main contribution on the carrier concentration is given by n_i ($n \approx N_d^+ + p \approx n_i$), as we can also see from figure 8 and figure 9. In fact at too high temperature, the concentration is essentially given by the intrinsic one (n_i), making the doping useless.

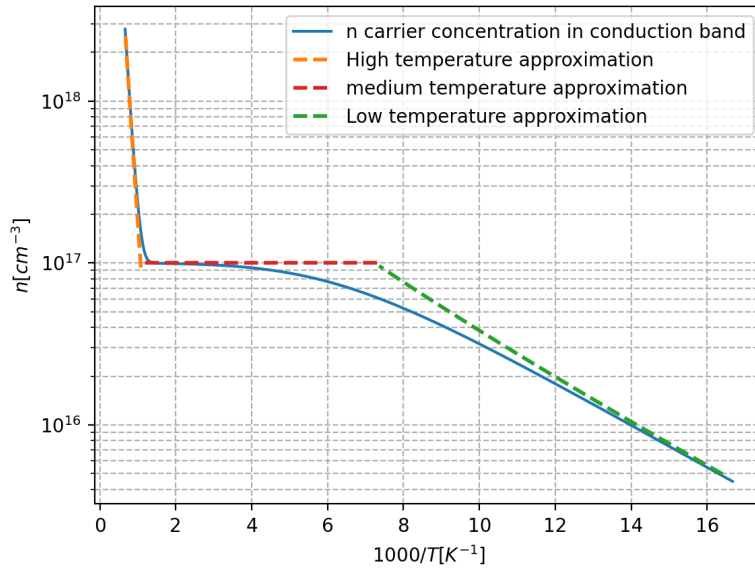


Figure 9: This figure shows the carrier concentration n and the different approximation of it in the 3 different regions