Chapter 2: Theory

2.1 The electronic properties of graphene

In this section, I delve into the linear band structure of graphene and derive its density of states. Using the density of states, I calculate the thermally excited electron and hole densities in graphene. We use this calculation in Ch. 4 to compare the carrier density in our graphene samples with the lowest achievable carrier density at room temperature.

2.1.1 Graphene's unique band structure

Graphene consists of a single layer of carbon atoms in a hexagonal lattice. The band structure of graphene is well-described by a tight binding model, where only hopping energy between nearest neighbor atoms is considered [22]. From the tight binding model, the dispersion relation of graphene is

$$E(k_x, k_y) = \pm t \left(3 + 2\cos(\sqrt{3}k_x a) + 4\cos(\frac{3}{2}k_y a)\cos(\frac{\sqrt{3}}{2}k_x a) \right)^{1/2}, \qquad (2.1)$$

where $k = (k_x, k_y)$ is the momentum vector of electrons in the graphene, $t = 2.8\ eV$ is the nearest-neighbor hopping energy, and $a = 1.42$ Å is the distance between the two nearest neighbor atoms. Figure 2.1 (a) shows a plot of the band structure given by Eq. 2.1.

In charge-neutral graphene, the Fermi energy E_F (the energy of the highest filled state

(a)

(b)

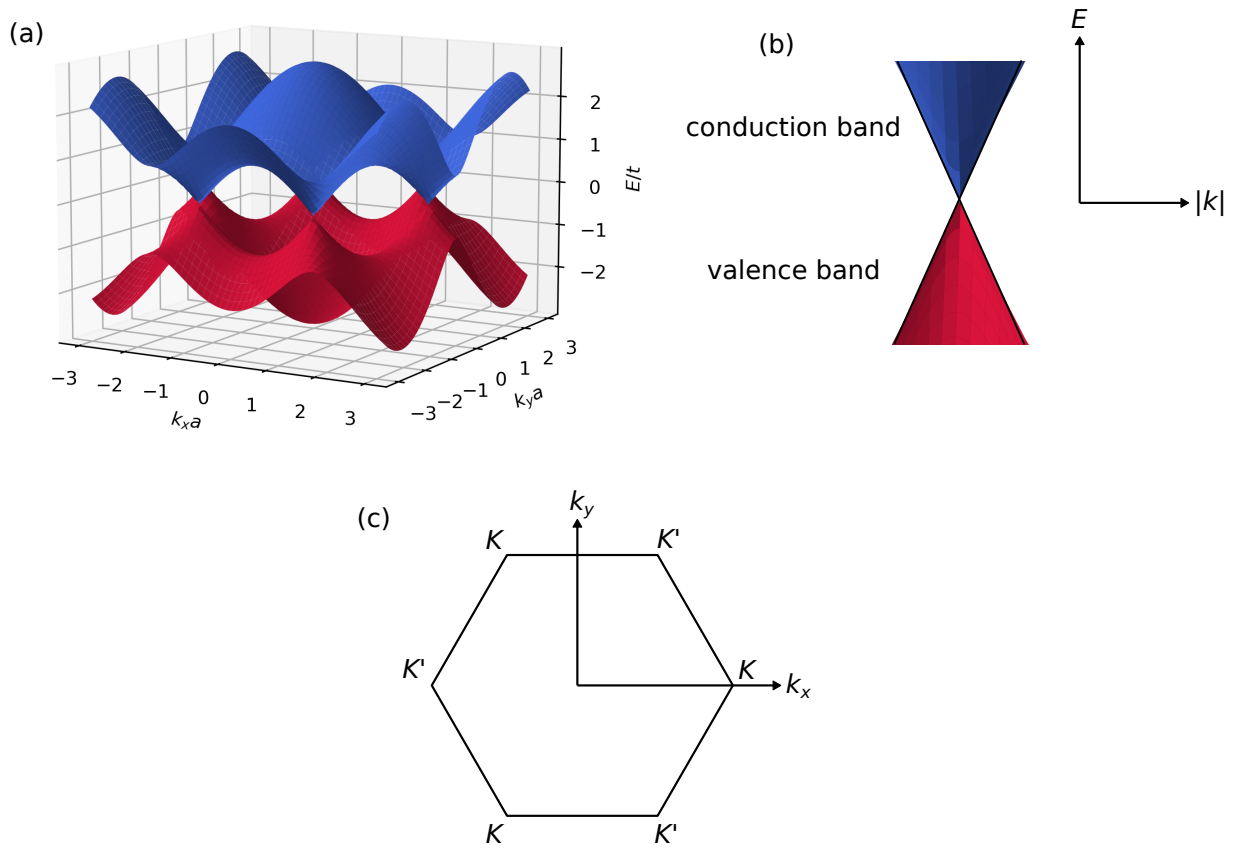conduction band

valence band

E

$|k|$

(c)

Figure 2.1: (a) A plot of graphene's dispersion relation given by Eq. 2.1. (b) Near the Dirac points, the energy of electronic states in graphene is approximately linear with respect to momentum. (c) The momentum-space lattice of graphene, with Dirac points labelled.

at zero temperature) intersects the bands at symmetry points called the K and K' points, also known as the Dirac points (Figure 2.1 (c)). Near the Dirac points, graphene's dispersion relation is linear, and can be approximated as

$$E(k) \approx \pm \hbar v_f |k|, \qquad (2.2)$$

where $\hbar$ is the reduced Planck's constant and $v_f = 3ta/2 \approx 10^6$ m/s is the Fermi velocity. Figure 2.1 (b) offers a magnified view of graphene's band structure near a Dirac point, showing its characteristic shape commonly referred to as the "Dirac cone". In conventional semiconductors and metals, we expect a parabolic energy-momentum relation of $E(k) = k^2/2m$, which gives a velocity of $v = \sqrt{2E/m}$. However, in the case of graphene, electrons near a Dirac point move at a velocity v_F which is independent of both energy and momentum, leading to many unique electronic properties [23]. For example, electrons and holes in graphene behave almost identically, in contrast to other materials [24, 23]. In the context of this dissertation, electron-hole symmetry is the most pertinent consequence of graphene's unique band structure.

In graphene, we can tune the Fermi energy using an electric field, which in turn tunes the charge carrier density.[1] Figure 2.2 illustrates graphene's band structure at zero temperature for $E_F < 0$, $E_F = 0$, and $E_F < 0$. When E_F lies above the Dirac point ($E_F > 0$), states in the conduction band are filled with electrons up to E_F (Fig. 2.2 (a)). Conversely, when $E_F < 0$, the valence band is depleted of electrons down to E_F (Fig. 2.2 (c)). These vacant electronic states, referred to as "holes", act as positively-charged quasiparticles. Similar to

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[1]The term "charge carrier" is commonly used to refer to both electrons and holes, and I use it in this context throughout this dissertation.
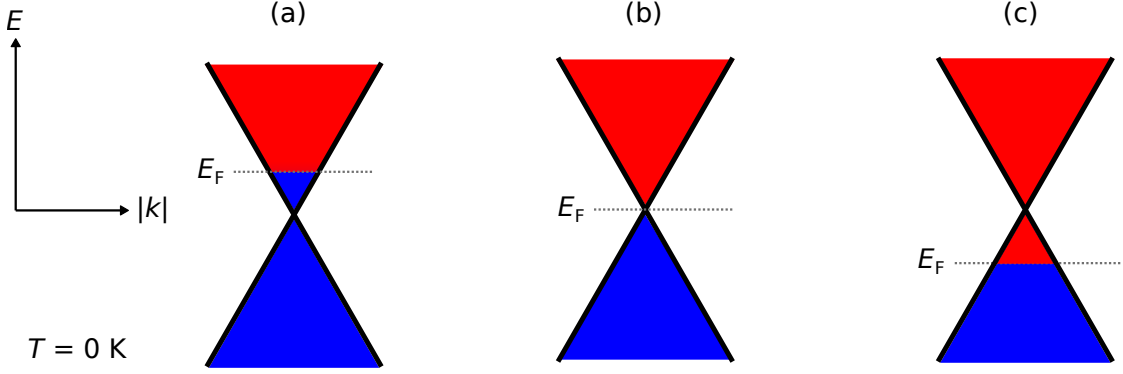
Figure 2.2: Filling of electronic states in graphene at zero temperature for (a) $E_F > 0$, (b) $E_F = 0$, and (c) $E_F < 0$. The colors indicate filled electronic states (blue, electrons) and vacant electronic states (red, holes).

electrons in the conduction band, holes in the valence band are free from the graphene lattice and can move in response to an electric field. In the case of charge neutral graphene ($E_F = 0$) at zero temperature, the conduction band is entirely empty, and the valence band is completely occupied, so no charge carriers should be present to conduct current (Fig. 2.2 (b)). However, in real graphene samples, charge carriers can still be present when $E_F = 0$, leading to finite conductivity when E_F is tuned to the charge neutrality point.

In real-world graphene samples, extrinsic sources of charge, referred to as electrostatic disorder, can be present. For instance, substrates like SiO_2 contain charge traps which induce spatially-varying charge carrier concentrations in graphene [25]. This substrate-induced disorder can be minimized by encapsulating graphene in hexagonal boron nitride (hBN) [26]. However, .even the most pristine encapsulated graphene samples exhibit some DC conductivity at the charge neutrality point [27] due to thermally-excited electrons and holes. To quantify the densities of these thermally excited electrons and holes, I will proceed to derive the density of states in graphene.
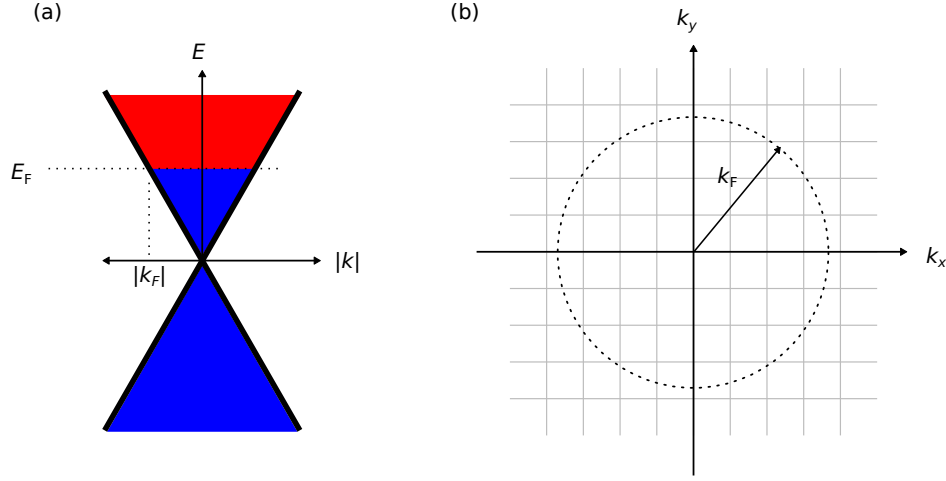
(a)

(b)

Figure 2.3: (a) Graphene band diagram with the Fermi energy indicated by E_F. (b) The k_x - k_y plane at $E = E_F$. The intersection of the Dirac cone with this plane forms a circle with radius $|k_F|$.

2.1.2 Density of states in graphene

The density of states helps us understand how many states are available for electrons to occupy at a certain energy level.

Consider a sheet of graphene at zero temperature in which we have tuned the Fermi energy E_F to lie above the Dirac point, filling the states in the conduction band with electrons to an energy E_F. Figure 2.3 (b) illustrates the k-plane slice at $E = E_F$, where the momentum at which E_F intersects the Dirac cone is defined as k_F. To find the density of states, we can count the number of states that lie inside this circle (states with momentum $0 < k < k_F$), and divide this number by the area of a single state in momentum space.

The graphene lattice is periodic, so the spatial part of the electron wavefunction must also be periodic. If the graphene real space periodicity is L (or, the unit cell has area L^2 in real space), then the allowable momenta are integer multiples of $(k_x, k_y) = (2\pi/L, 2\pi/L)$.

Thus, a single occupied state takes up an area of $(2\pi/L)^2$ in momentum space. The total number of states with $k < k_F$ is given by the area of our circle of radius k_F divided by the area of a single state,

$$N = \frac{\pi k_F^2}{(2\pi/L)^2} = \frac{k_F^2 L^2}{4\pi}. \tag{2.3}$$

Then, the density of states is given by

$$D(E_F) = \frac{4}{L^2}\frac{\mathrm{d}N}{\mathrm{d}k_F} = 4\frac{(2k_F)}{4\pi} = \frac{2|E_F|}{\pi\hbar^2 v_F^2}, \tag{2.4}$$

where the factor of 4 originates from graphene's four-fold degeneracy of two valleys (K and K') and two spins (spin up and spin down), and the absolute value ensures that $D(E)$ is a positive quantity. Equation 2.4 elucidates why graphene is a semimetal — though graphene has no band gap, the density of states is zero at the Fermi energy in charge-neutral graphene. However, thermal energy can excite charge carriers to occupy states that are not at the Fermi energy.

2.1.3   Thermally excited charge carriers in graphene at finite temperature

At finite temperatures, electrons will be thermally excited into the conduction band, leaving holes in the valence band. These thermally excited electrons and holes can contribute to conduction, and limit the lowest achievable carrier density (and lowest achievable conductance) in charge-neutral graphene at finite temperature. The thermally excited electron and hole densities n and p are given by

$$n = \int_0^\infty f(E)D(E)\mathrm{d}E, \tag{2.5}$$

$$p = \int_{-\infty}^0 (1 - f(E))D(E)\mathrm{d}E, \tag{2.6}$$

where $f(E)$ is the Fermi occupation function, which takes the form

$$f(E) = \frac{1}{1 + \mathrm{e}^{E/k_B T}}, \tag{2.7}$$

where k_B is Boltzmann's constant and T is temperature. I take $E_F = 0$ to reflect charge neutral graphene.

Equations 2.5 and 2.6 can be solved analytically as follows:

$$\begin{aligned}
n = \int_0^\infty f(E)D(E)\mathrm{d}E &= \int_0^\infty \frac{1}{1 + \mathrm{e}^{((E)/k_B T)}} \frac{2|E|}{\pi \hbar^2 v_F^2}\mathrm{d}E \\
&= \frac{2(k_B T)^2}{\pi \hbar^2 v_F^2} \int_0^\infty \frac{x}{1 + \mathrm{e}^x}\mathrm{d}E \\
&= \frac{2(k_B T)^2}{\pi \hbar^2 v_F^2} \frac{\pi^2}{12},
\end{aligned} \tag{2.8}$$

$$\begin{aligned}
p = \int_{-\infty}^0 (1 - f(E))D(E)\mathrm{d}E &= \int_{-\infty}^0 \left(1 - \frac{1}{1 + \mathrm{e}^{((E)/k_B T)}}\right) \frac{2|E|}{\pi \hbar^2 v_F^2}\mathrm{d}E \\
&= \frac{2(k_B T)^2}{\pi \hbar^2 v_F^2} \int_{-\infty}^0 \left(x - \frac{x}{1 + \mathrm{e}^x}\right)\mathrm{d}E \\
&= \frac{2(k_B T)^2}{\pi \hbar^2 v_F^2} \frac{\pi^2}{12},
\end{aligned} \tag{2.9}$$

where I use the substitution $x = E/(k_B T)$ to evaluate the integral. Both n and p yield identical expressions, which is consistent with the symmetry of graphene's band structure above and below $E = 0$ near the Dirac point. From Eqs. 2.8 and 2.9, I calculate the minimum achievable carrier density at $T = 300$ K to be 0.16×10^{12} cm^{-}2.