PART B
CHAPTER 5

INTRODUCTION TO PHYSICS OF GRAPHENE
5.1 Introduction

After the experimental discovery in 2004 by Novoselov et al [5.1], graphene has become an important electronic material, ushering in a tremendous outburst of scientific activity in the study of its electronic properties which continues till today. Due to flexibility of its bonding, carbon based systems show different structures such as, graphite, fullerene, carbon nanotube, monolayer graphene, bilayer graphene and graphene nanoribbons. As such 2D graphene rolled up in the plane is a carbon nanotube, and a multilayer stacks of graphene with week interlayer coupling forms graphite. All these structures exhibit different physical properties as a result of dimensionality of their structures.

Graphene is a monoatomic 2D sheet of carbon atoms arranged in a honeycomb lattice, now largely known as monolayer graphene (MLG). The $sp^2$ hybridization between one s orbital and two p orbitals leads to a trigonal planar structure with the formation of a σ bond between carbon atoms that are separated by 1.42Å. One of the most interesting aspects of the graphene is that its low-energy excitations are massless, chiral and Dirac Fermions [5.2]. The dispersion relation is linear with the Fermi velocity $v_F$ of Dirac Fermions 300 times smaller than the speed of light c. Graphene is a zero gap semiconductor with its chemical potential crossing exactly at the Dirac point in neutral graphene. Because of the two atoms per unit cell, the electrons and holes have chiral nature, which has major impact on its transport properties. This has also led to the experimental observation of many interesting effects similar to those predicted in the relativistic regime. When subjected to magnetic fields, Dirac Fermions behave in unusual ways compared to ordinary electrons, leading to new physical phenomena such as anomalous integer quantum hall effect (IQHE) [5.1,5.3, 5.4]. Besides, in an intrinsic graphene, highest
room temperature mobility $\sim 2 \times 10^5 \text{cm}^2/\text{Vs}$ has been predicted [5.5] and observed [5.6], due to weak electron-phonon coupling, making it a potential candidate for its applications in high speed devices.

Graphene has immense potential to be a key ingredient of new devices, such as single molecule gas sensors, ballistic transistors and spintronic devices [5.2]. The electronic properties of graphene can also be exploited for the creation of graphene-based systems with magnetic and superconducting properties. Although the graphene field is still in its early stages, the scientific and technological possibilities of this new material seem to be unlimited. The understanding of the electronic properties of graphene has opened doors for new frontiers in electronics.

Bilayer graphene (BLG), which consists of two weakly coupled stacked monolayers and where the quasi particles are massive chiral fermions, has a quadratic low-energy band structure gives rise to very different scattering properties from those of the monolayer [5.7]. However, BLG has many common physical properties with the MLG, such as the high electron mobility and high mechanical stability. It also presents the unique property that a tunable band gap can be opened and controlled easily by applying a potential difference between the two layers or by external dopants. Because of the tunable energy gap BLG has an edge over MLG making it as most promising material for its application in the fabrication of graphene transistors, tunnel barriers and quantum dots. These properties have made bilayer graphene a subject of intense interest.

5.2 Graphene

5.2.1 Monolayer graphene

Monolayer graphene has been described as the most perfect 2D electronic material possible in nature, as it is exactly one atomic monolayer thick, besides its
carrier dynamics being confined to this strict 2D layer. The two equivalent lattice sites [A and B in Fig. 1(a)] in the 2D hexagonal lattice give rise to the "chirality".

**Figure 1:** (a) Graphene hexagonal lattice. Different colors show two triangular sublattices. Brillouin zone of the graphene in momentum space is shown on the right. Figures are adapted from [5.2].

MLG has a triangular lattice structure with basis of two atoms per unit cell with the 2D lattice vectors \( \mathbf{A}_0 = (a/2)(3, \sqrt{3}) \) and \( \mathbf{B}_0 = (a/2)(3, -\sqrt{3}) \) (\( a=0.142 \text{nm} \) is the carbon-carbon distance). \( \mathbf{K} = (2\pi/(3a), 2\pi/(3\sqrt{3}a)) \) and \( \mathbf{K}' = (2\pi/(3a), -2\pi/(3\sqrt{3}a)) \) are the inequivalent corners of the Brillouin zone and are called Dirac points. These Dirac points are of great importance in the electronic transport of graphene, and play a similar role of \( \Gamma \) points in direct band-gap semiconductors such as GaAs [5.2, 5.8].

The energy dispersion of MLG [Fig. 2(a)], the most important aspect, is its linear energy momentum relationship with the conduction and valence bands intersecting at \( k = 0 \), with no energy gap. Graphene is thus a zero band-gap semiconductor with linear long-wavelength energy dispersion for electrons (holes) in the conduction (valence) bands. A valley degeneracy \( g_v = 2 \) arises due to two Dirac points at \( K \) and \( K' \), where the Dirac cones for electrons and holes touch [Fig. 2(b)] each other in momentum space.
5.2.2 Hamiltonian, eigen states and energy eigen values in MLG

In the continuum limit and in the effective mass approximation, the Hamiltonian in the vicinity of the K point is [5.10, 5.11]

$$H_K(k) = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \sigma \cdot k ,$$

(5.2.2.1)

where the $\sigma = (\sigma_x, \sigma_y)$ is a vector of Pauli matrices. The wave functions of these relativistic-like (Dirac) particles have spinor structure. For the K and K' points, the wave functions are given by
\[
\Phi_x^k = \frac{e^{ikr}}{\sqrt{A}} \begin{pmatrix} s \\ e^{i\theta_k} \end{pmatrix} ; \quad \Phi_x^k = \frac{e^{ikr}}{\sqrt{A}} \begin{pmatrix} e^{i\theta_k} \\ s \end{pmatrix},
\]
\hspace{1cm} (5.2.2.2)

where \( k(r) \) is 2D wave (position) vector, \( s = +1 \) for the upper band (electrons) and -1 for lower band (holes), \( \tan \theta_k = k_x/k_0 \) and \( A \) is the area of the graphene.

The corresponding low energy eigenvalues are described by the linear energy dispersion around the K points

\[
E_k = \hbar v_F k, \quad \text{with} \quad k = |k|
\]
\hspace{1cm} (5.2.2.3)

where \( v_F \), called Fermi velocity, is material constant. The best approximate value for \( v_F \approx 10^6 \text{ m/s} \) is independent of the carrier density, therefore dispersion corresponds to two cones meeting at the K point (Fig. 2). The unique band structure of graphene, described above, brings about profound changes in the electronic properties of the system.

The density of states \( D(E_k) \) counts the number of quantum states in unit energy range per unit area in the vicinity of a fixed energy \( E_k \). It may be obtained from

\[
D(E_k) = g_s g_v \sum_k \delta(E - E_k) \]
\hspace{1cm} (5.2.2.4)

with \( g_s = g_v = 2 \) taking account of spin \( (g_s) \) and valley \( (g_v) \) degeneracy, respectively. Converting the summation to integration, in the vicinity of the Dirac points, the integral may be evaluated easily because of isotropy of the energy dispersion. One obtains [5.2],

\[
D(E_k) = \frac{g_s g_v |E_k|}{2\pi \hbar^2 v_F^2}, \]
\hspace{1cm} (5.2.2.5)

showing \( D(E_k) \sim E_k \), contrary to its constant value in conventional 2DEG systems.
5.2.3 Bilayer graphene

Bilayer graphene can be described as the two weakly coupled MLGs by interlayer carbon hopping. Even though it shares some of the characteristics from both the MLG and the traditional 2DEG system, it is a unique complex system, different from each of them. The low-energy band structure and the formation of a band gap at the K point when a transverse electric field is applied are experimentally determined by Ohta et al [5.12]. Besides, its associated effective mass, the chiral nature of the charge carriers is manifested in the Berry’s phase and other properties.

Figure 3: Lattice structure of BLG. $\gamma_0$ and $\gamma_1$ are, respectively, the intralayer and interlayer hopping parameters. The other interlayer hopping parameters $\gamma_2$ and $\gamma_4$, being much smaller than $\gamma_1$, are normally neglected [5.13].

Figure 4: (a) Band structure of BLG for potential between the two layers $V = 0$. (b) The energy band close to the neutrality point K is shown enlarged for different values of V [5.14].
In BLG the effects of chirality can be distinguished from those of the Dirac spectrum in MLG and traditional 2DEG.

5.2.4 Hamiltonian, eigen states and energy eigen values in BLG

In bilayer graphene the effective Hamiltonian is now well known [5.15-5.19]. In the low energy regime, the effective Hamiltonian of BLG is reduced to the (2 x 2) matrix form and is given by [5.15]

\[ H_0 = \frac{1}{2m} \begin{pmatrix} 0 & (k_x - ik_y)^2 \\ (k_x + ik_y)^2 & 0 \end{pmatrix}, \]

(5.2.4.1)

where \( m = 2\gamma_1 \hbar^2 / (3\gamma_0 a^2) \approx 0.033m_e \), \( \gamma_0 \approx 3.16eV \) is the in-plane coupling, \( \gamma_1 \approx 0.39eV \) is the out-of-plane coupling, \( a \approx 0.246 \text{ nm} \) is the lattice constant and \( m_e \) is the electron mass.

The wave function for the Hamiltonian (Eqn.5.2.4.1) is given by

\[ \psi_{\mathbf{k}}^s = e^{i\mathbf{k}\mathbf{r}} (e^{-2i\theta_k}, s) / \sqrt{2A}, \]

(5.2.4.2)

and the corresponding energy eigen value is given by,

\[ E_{\mathbf{k}} = \hbar^2 k^2 / 2m, \]

(5.2.4.3)

where \( \theta_k = \tan^{-1}(k_y/k_x) \) and \( s = \pm 1 \) denote the band index.

Since BLG has parabolic dispersion relation (Eqn.5.2.4.3), its DOS is similar to the conventional 2D semiconductor system [5.8]. It is given by,

\[ D(E_k) = \frac{g_x g_y m}{2\pi \hbar^2}, \]

(5.2.4.4)

which is independent of \( E_k \).

Electrons distribution in graphene is assumed to be Fermi-Dirac statistics \( f^0(E_k) \) with \( E_F = h\nu_F k_F \) in MLG and \( E_F = \hbar^2 k_F^2 / 2m \) in BLG with \( k_F = (\pi n_e)^{1/2} \).
5.3 Scattering mechanisms in graphene

The transport properties of graphene as a function of temperature and carrier density have been of key fundamental and technological interest. There exist studies of important scattering mechanisms which govern the transport properties by comparing calculations with the existing experimental data [5.2, 5.8]. The scattering mechanisms that limit the transport properties are charged impurities [5.20, 5.21] located near the interface between graphene and the substrate, vacancies inducing midgap states [5.21] and acoustic phonons [5.5, 5.21] and optical phonons [5.22]. Hwang and Das Sarma [5.5] have calculated the intrinsic mobility limited by only acoustic phonon scattering and mobility exceeding $10^5 \text{cm}^2/\text{V} \cdot \text{s}$ is found feasible. Moreover, the scattering due to interface roughness [5.22] and surface polar phonons [5.23] are shown to be other important scattering mechanisms. Due to the high optic phonon energy [~200meV] and nonionic bonding, optical phonon scattering and piezoelectric scattering is negligible up to room temperature [5.24]. Scattering due to acoustic phonons and optical phonons are called intrinsic scattering and all other mechanisms are called extrinsic scattering mechanisms.

Recently, the study of carrier transport in a two-dimensional bilayer graphene (BLG) has become the subject of intense interest. Experimental results indicate that the mobility of the charge carriers in BLG is smaller than MLG [5.8]. The Scattering mechanisms considered in BLG are acoustic phonons [5.5, 5.21], charged impurity (long range Coulomb) [5.25] and short range disorder [5.25] and surface polar phonon scattering [5.26, 5.27]. Figure 5 depicts the various scattering mechanisms that govern the transport properties of monolayer and bilayer graphene.
Figure 5: Scattering mechanisms in monolayer and bilayer graphene.

The scattering due to these various mechanisms described above depends upon the temperature, disorder concentrations and significance of each mechanism is different in graphene systems. In order to find the key scattering mechanisms that dominate in different temperature range, the knowledge of the transition probability of an electron from initial state \((k)\) to the final state \((k')\) is essential. The transition rate from the quantum state \(k\) to \(k'\) is approximated by the Fermi’s Golden rule

\[ S(k, k') = \frac{2\pi}{\hbar} |\langle k | V_{\text{scat}} | k' \rangle|^2 \delta(E_k - E_{k'}). \] (5.3.1)
where $|<k|V_{\text{scat}}|k'>$ is the scattering matrix element.

### 5.3.1 Charged impurity scattering in monolayer graphene

In graphene sheets on polar substrates like SiO$_2$, SiC etc the charged impurities reside in the substrate layer and are screened by the conduction electrons of the graphene sheet. Employing the Thomas-Fermi approach the screened potential inside the graphene sheet is given by [5.21],

$$\varphi(q) = \frac{Ze}{2\epsilon_0} \frac{e^{-q\epsilon_x}}{q + \gamma}, \quad (5.3.1.1)$$

where $\gamma = D(E_k)e^2/2\epsilon_0\epsilon_s$, $Ze$ is the charge of the ionized impurity, $D(E_k)$ is the density of states given by Eqn. (5.2.2.5), $\epsilon_s$ is the permeability of the substrate and $z_c$ is the shortest distance of the external charged impurity to the two-dimensional graphene sheet.

The relaxation time $\tau(E_k)$ due to impurity scattering is given by [5.28]

$$\frac{1}{\tau(E_k)} = \frac{N_i \sum_k S(k,k')G(\theta)(1 - \cos \theta)}{N_i \sum_k S(k,k')G(\theta)(1 - \cos \theta)} \quad (5.3.1.2)$$

where $N_i$ is the number of charged impurities, $S(k,k')$ is the transition rate and $G(\theta)=[1+\cos(n\theta)]/2$ is a wave function form factor associated with the chiral nature of graphene with $n=1$ (2) for MLG (BLG) and $\theta = \theta_k - \theta_{k'}$ is the angle between $k$ and $k'$.

Using the matrix element and $S(k,k')$ in Eqn. (5.3.1.2), the relaxation time due to charged impurities (coulomb potential) is given by [5.21]

$$\tau_{\text{imp}}(E_k) = hE_k / u_0^2 \quad , \quad (5.3.1.3)$$

where
\[ u_o = \frac{\sqrt{n_i^c Ze^2}}{4\varepsilon_0 e(1 + \gamma')} \quad \gamma' = \gamma \hbar \nu_f / E_k, \quad (5.3.1.4) \]

and \( n_i^c (= N_i/A) \) is the density of charged impurities in the sample.

### 5.3.2 Vacancy scattering in monolayer graphene

Vacancies, cracks or boundaries in the graphene sheet give rise to bound states at the Dirac point, so called midgap states [5.2]. In order to incorporate the effect of midgap states in the calculation of the relaxation time, phase shift induced by the scattering center should be considered. The scattering from vacancies leads to the following phase shift,

\[
\delta_k = -\frac{\pi}{2} \frac{1}{\ln(kR_o)}, \quad (5.3.2.1)
\]

for \( kR_o \ll 1 \) with \( R_o \) being the radius of the vacancies.

The relaxation rate due to vacancies is given by [5.21]

\[
\tau_{vac}(E_k) = \frac{\hbar \rho(E_k)}{2 \pi n_i} \left(\ln(kR_o)\right)^2, \quad (5.3.2.2)
\]

where \( n_i \) is the impurity concentration due to vacancies.

### 5.3.3 Surface roughness scattering in monolayer graphene

Surface roughness scattering is assumed to arise from the rippling of the graphene sheet after it is deposited on the oxidized substrate. The autocorrelation function for the random potential is taken to be same as in conventional 2D heterostructures [1.40].

The relaxation rate due to surface roughness scattering is given by [5.22]

\[
\frac{1}{\tau_{SR}(E_k)} = \frac{2k}{\nu_f} \left(\frac{\Lambda n_i e^2 \Delta}{8\pi \hbar \varepsilon_0}\right)^2 \frac{1}{\sqrt{1 + k^2 \Lambda^2}} \exp\left(\frac{k\Lambda}{\sqrt{1 + k^2 \Lambda^2}}\right), \quad (5.3.3.1)
\]
where $\Delta$ is the root mean square height, $n_s$ concentration and $\Lambda$ is the correlation length for surface roughness.

5.3.4 Charged impurity scattering in bilayer graphene

Ionized impurities in the substrate cause scattering of electron in BLG, similar to the case of MLG (section 5.3.1). The matrix element for screened coulomb charged impurity is given by [5.25]

$$N_i |< \mathbf{k}| V_{\text{scat}} | \mathbf{k}' > |^2 = n_s |u_i|^2 = n_s V_i(q) / \varepsilon(q)^2.$$  \hspace{1cm} (5.3.4.1)\]

The relaxation time due to charged impurity scattering is found to be [5.25, 5.27],

$$\frac{1}{\tau_{\text{IMP}}(E_k)} = \frac{m n_s^2}{2 \pi \hbar^2} \int_0^{2\pi} V_i(q)^2 \left[ \frac{e^{-2qd} + e^{-2qd+c}}{2} \right] G(\theta) [1 - \cos(\theta)] d\theta,$$  \hspace{1cm} (5.3.4.2)

where $d (=0.4nm)$ is the distance between the first layer and the substrate, $c (=0.34nm)$ is the interlayer distance, $V_i(q) = e^2 / 2\varepsilon_0 \varepsilon_r q$, is the 2D coulomb potential. $\varepsilon(q) = [1 + (q_{TF}^2 / q)]$ is the dielectric screening function [5.8, 5.29] and $q_{TF} = m e^2 / \pi \hbar^2$ is the 2D Thomas-Fermi screening wave vector.

5.3.5 Short range disorder scattering in bilayer graphene

In BLG, short range disorder scattering is very important as it contributes highly for linearly increasing conductivity with increase in carrier density [5.25]. The expression for matrix element for short range disorder scattering is given by [5.25]

$$N_i |< \mathbf{k}| V_{\text{scat}} | \mathbf{k}' > |^2 = n_d V_0^2,$$  \hspace{1cm} (5.3.5.1)

where $n_d$ is the density of short-ranged impurities and $V_0$ is the strength of the short-range potential. The expression for relaxation time due to short-range disorder scattering is given by [5.25]
1 \frac{1}{\tau_{SRD}(E_k)} = \frac{m}{2\pi\hbar^2} \int_0^\pi n_d V_0^2 G(\theta)[1 - \cos(\theta)]d\theta, \tag{5.3.5.2}

where the product $n_d V_0^2$ is the strength of the short-ranged disorder potential.

5.3.6 Acoustic phonon scattering via deformation potential in monolayer and bilayer graphene

The atomic vibrations give rise to propagation of lattice waves in graphene leading to acoustic and optical branches. The acoustic wave is represented by the displacement $u_q = A_q \exp(i(q \cdot r - \omega_q t))$, where $|A_q|^2 = (\hbar/2 \rho A_\omega q) N_q^0$ with frequency $\omega_q = \nu_s q$, wave vector $q$ and velocity $\nu_s$. $N_q^0 = (\exp(\hbar \omega_q/k_B T) - 1)^{-1}$ is the phonon Bose distribution function at lattice temperature $T$ and $\rho$ is the areal mass density of the graphene [5.21]. The acoustic phonons are of purely 2D in nature.

The potential due to propagating acoustic wave has the form $U_s = K_q u_q$, where $|K_q|^2 = \Xi_s^2 q^2$, $\Xi_s$ is deformation potential coupling constant [5.21]. In graphene, the electron coupling with acoustic phonons is via deformation potential and hence only longitudinal acoustic phonons will involve in the scattering of electrons.

The scattering rate due to acoustic phonons is given by

$$ S(k, k') = \frac{2\pi}{\hbar} |M(k, k')|^2 G(\theta)(N_q^0 + 1/2 \pm 1/2) \delta(E_{k'} - E_k \pm \hbar \omega_q), \tag{5.3.6.1} $$

The corresponding matrix element for electron scattering is given by [5.5, 5.21]

$$ |M(k, k')|^2 = \hbar \Xi_s^2 q / 2 \rho A \nu_s. \tag{5.3.6.2} $$

The relaxation time due to acoustic phonon scattering, without screening, for MLG is shown to be [5.30]
\[
\frac{1}{\tau_{dp}(E_k)} = \frac{A}{2\pi \hbar^3 v_F^2} \int_0^{2\pi} \frac{(1 - \cos \theta) |M(k,k'))|^2}{f^0(E_k)[1 - f^0(E_k)][N_q^0(E_k + \hbar \omega_q)[1 - f^0(E_k + \hbar \omega_q)]f^0(E_k)]}
\]

\[
\left\{ \left[ N_q^0(E_k + \hbar \omega_q)[1 - f^0(E_k + \hbar \omega_q)]f^0(E_k) \right] + \left[ N_q^0(E_k - \hbar \omega_q)[1 - f^0(E_k - \hbar \omega_q)]f^0(E_k) \right] \right\} \quad (5.3.6.3)
\]

In the equipartition regime ($\hbar \omega_q \ll k_B T$) the above equation reduces to [5.5, 5.21]

\[
\tau_{dp}(E_k) = \frac{8 \hbar^3 \rho v_F^2}{\Sigma_d^2 k_B T E_k} \quad (5.3.6.4)
\]

In BLG, electron scattering by acoustic phonons is again via deformation potential coupling and the corresponding relaxation time, without screening, is shown to be [5.31]

\[
\frac{1}{\tau_{dp}(E_k)} = \frac{m \Sigma_d^2}{\pi \hbar^3 \rho v_F} \int \frac{q dq}{\sqrt{k(1 - (q/2k)^2)} \sqrt{1 - f^0(E_k)}} \left[ N_q^0[1 - f^0(E_k + \hbar \omega_q)] + (N_q^0 + 1)[1 - f^0(E_k - \hbar \omega_q)] \right] \quad (5.3.6.5)
\]

5.3.7 Surface polar phonon scattering in monolayer and bilayer graphene

When graphene is on the top of a polar substrate the charge carriers are in close proximity with the surface of the substrates. Vibrations of the substrate ions with the opposite charge polarity give rise to 2D surface polar phonons (SPPs) and produce an electric field which decays exponentially away from the surface of the substrate. Electrons in the graphene which are in the proximity of the surface can feel this electric field and will be scattered by SPPs. This can result in significant reduction in the low field mobility [5.23, 5.24, 5.32]. Due to inelastic nature of SPP, they provide another channel for current saturation, besides intrinsic optical phonons.

The matrix element for the electron scattering due to SPPs in MLG is given by [5.23]
where $q = |k' - k|$ is the wave vector of SPPs, $\theta$ is the scattering angle, $F^2 = (\hbar \omega_s / 2 A \varepsilon_0)[(1 / (\varepsilon_s^\infty + 1)) - (1 / (\varepsilon_s^0 + 1))]$ is electron phonon coupling parameter with $\varepsilon_s^0$ ($\varepsilon_s^\infty$) is the low (high) frequency dielectric constants of the substrate and $d$ is the distance of the graphene sheet from the substrate.

The relaxation time for electron scattering due to SPPs in MLG is given by \[5.23\]

\[
\frac{1}{\tau_{\text{SPP}}(E_k)} = \frac{2\pi}{\hbar} \sum_q e^2 F^2 q \left[ \frac{e^{-2qd}}{q} \right] \left( N_q^0 + \frac{1}{2} \right) G(\theta) \delta(E_{k'} - E_k \pm \hbar \omega_s),
\]

where $N_q^0 = (e^{\hbar \omega_s / kT} - 1)^{-1}$ is the phonon Bose distribution function and $\hbar \omega_s$ is the SPP energy (with $s = 1$ and 2 of two SPPs of different energy).

The respective matrix element due to SPP in BLG is given by \[5.27\],

\[
|M(k,k')|^2 = e^2 F^2 \left[ \frac{e^{-2qd} + e^{-2q(d+c)}}{2q} \right].
\]

In BLG, the relaxation time due to SPP scattering is \[5.27\],

\[
\frac{1}{\tau_{\text{SPP}}(E_k)} = \frac{2\pi}{\hbar} \sum_q e^2 F^2 q \left[ \frac{e^{-2qd} + e^{-2q(d+c)}}{2q} \right] \left( N_q^0 + \frac{1}{2} \right) G(\theta) \delta(E_{k'} - E_k \pm \hbar \omega_s).
\]

The scattering matrix elements and relaxation rates mentioned above will be used, in the successive Chapters, for the calculation of diffusion thermopower in MLG, electronic thermal conductivity and hot electron energy loss rates in BLG.

In the present study, the Fermi energy is taken to be away from the Dirac points in the conduction band and hence electrons are the only charge carriers being considered in the calculations of the transport properties undertaken.
References:


