

# Carrier relaxation time modelling of monolayer black phosphorene

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Phosphorene as an innovative structure that can be exfoliated similarly to the graphene with a direct, inherent and suitable bandgap presents exceptional prospects for future generations of electronic devices. Phosphorene possess high carrier mobility, therefore, in this work its carrier statistics in the form of monolayer phosphorene in the non-degenerate limit is analytically modelled and the mobility relation with carrier relaxation time is investigated. Energy dispersion relation is used to develop and calculate the required parameters for carrier relaxation time model which is an important parameter in conduction theory. On the other hand, the dependency of carrier velocity and mobility to voltage, normalised Fermi energy and temperature are modelled. Finally, the carrier relaxation time as a function of carrier mobility is modelled and its dependency towards temperature and normalised Fermi energy is discussed. It is shown that the relaxation time is strongly dependent on the carrier mobility which increases by increasing the mobility.

**1. Introduction:** To overcome the limitations of conventional silicon-based devices, numerous studies have been conducted on new two-dimensional (2D) monolayer materials for use in the next generation of electronic devices [1, 2]. One of the advantages of the phosphorene as a 2D material is ultra-thin structure which allows electrostatic control by a gate when implemented as a channel in field effect transistor geometry [3]. Due to their interesting electrical, chemical and optical characteristics, the 2D materials such as MoS<sub>2</sub> and graphene have been the subject of great interest [4–6]. However, some properties in single layer or a few layer materials are not demonstrated by their bulk counterparts, such as the massless Dirac fermion behaviour in graphene [7–9]. Graphene possess very high mobility of carriers (~20,000 cm<sup>2</sup>/V/s at room temperature) which enables it to reach ballistic transport at large length scales; but the lack of inherent finite energy bandgap severely limits its application in nanotransistors [2, 10]. Monolayer MoS<sub>2</sub> has a direct energy bandgap of 1.8 eV. The carrier mobility of monolayer MoS<sub>2</sub> has been reported to be ~200 cm<sup>2</sup>/V/s [11] and may reach up to 500 cm<sup>2</sup>/V/s [1]. However, a few recent experimental studies indicate that because of the capacitive coupling between the gates, the value of the mobility must be overestimated [12, 13], thus challenging its common application in electronics.

Most recently, phosphorene, a new 2D semiconducting material with a direct energy bandgap, has been successfully exfoliated from black phosphorus [14–16]. Black phosphorus is a layered three-dimensional material in which individual atomic layers are stacked by van der Waals interactions, similar to graphite [17]. Phosphorene is a single layer of phosphorus which has a puckered honeycomb structure where each atom is covalently bonded to three adjacent atoms [18–20], as shown in Fig. 1. The three bonds engage to all three electrons of phosphorus. Thus, unlike graphene [21, 22], phosphorene is a semiconductor with a direct bandgap of 0.9–2 eV at the *G* point of the first Brillouin zone [15, 23, 24]. The bandgap can be controlled by the number of layers. By adding each layer to a single layer, interlayer interactions reduce the bandgap and ultimately reach 0.3 eV [25–28] for bulk black phosphorus [15]. As a consequence, the direct bandgap moves to the *Z* point [29, 30]. Such a band structure enables its wide application in field effect transistor [15]. Therefore, phosphorene is a great candidate which can overcome the limitations of all other 2D materials for ultra-thin transistor structure, thereby revolutionising the electronic industry.

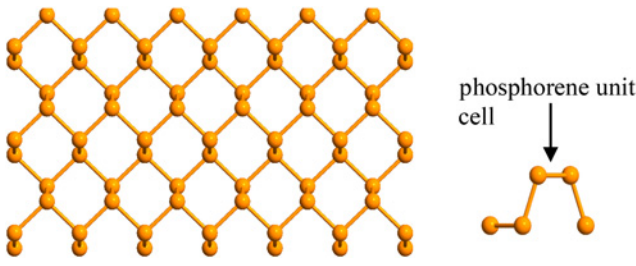
The phosphorene-based field effect transistor indicates relatively high carrier mobility of 286 cm<sup>2</sup>/V/s and remarkable high on/off ratio, up to 10<sup>4</sup> [10, 14]. The value of carrier mobility is dependent on thickness and can reach even 1000 cm<sup>2</sup>/V/s at ~10 nm thickness [15]. A recent experimental work demonstrated a hole mobility exceeding 650 cm<sup>2</sup>/V/s at room temperature along the light effective mass direction (*x*) and 1000 cm<sup>2</sup>/V/s at 120 K temperature [31]. Meanwhile, it has been reported that in bulk black phosphorus, electron and hole mobilities can exceed 1000 and 50,000 cm<sup>2</sup>/V/s at 300 and 30 K, respectively [32].

However, research on phosphorene is in its initial steps and demands wide and deep investigation of electrical and physical characteristics before implementing for industrial purpose. Thus, the behaviour of the carriers in phosphorene should be studied and analysed. Relaxation time is an important factor which plays prominent role in the conductivity of the semiconductors. Studying carrier relaxation time may guide us to evaluate the behaviour of the carriers in different aspects. In order to investigate carrier relaxation time, we should study the mobility and velocity of electrons first. In this Letter it is started with the energy dispersion relation to calculate the density of states and carrier density relations for further analysis. Then, the velocity and mobility of the electrons in non-degenerate regime for parabolic band energy and the electron relaxation time are modelled and investigated. The modelling mechanism is briefly explained and discussed step by step in the following sections.

**2. Results and discussion:** The dispersion relation of electrons through the whole Brillouin zone of the one-dimensional phosphorene is given by [33]

$$E(k_x) = E_g \pm \left( \frac{\hbar^2}{2m_0} - \frac{P_{x2}^2}{E_1} + \frac{P_{x1}^2}{E_g} \right) k_x^2 \quad (1)$$

where  $P_{x1} = (2\pi\hbar^2/m_0a_x)$ ,  $E_g$  is the bandgap at the  $\Gamma$ -point,  $\hbar$  is the reduced plank constant,  $P_{x1}$  and  $P_{x2}$  are the momentums in the *x* direction and  $E_1$  is the energy difference between neutrality points. As reported by Li and Appelbaum [33], the magnitude of the  $E_g + E_1 + E_2 \simeq 5$  eV. On the other hand,  $E_1$  is roughly equal to  $E_2$  which means for bandgap around  $E_g = 2$  eV [15], the magnitude of  $E_1$  is calculated to be  $E_1 = 1.5$  eV, and the magnitude of



**Fig. 1** Illustration of a monolayer phosphorene with puckered honeycomb structure

$P_{x2}$  which is roughly equal to  $E_1$  is extracted to be  $P_{x2} = 1.5$  eV. Based on the energy equation, the  $E$ - $k$  relation of the monolayer phosphorene is plotted as shown in Fig. 2 which indicates that the narrow width phosphorene as a one-dimensional material demonstrates parabolic band structure near the minimum energy.

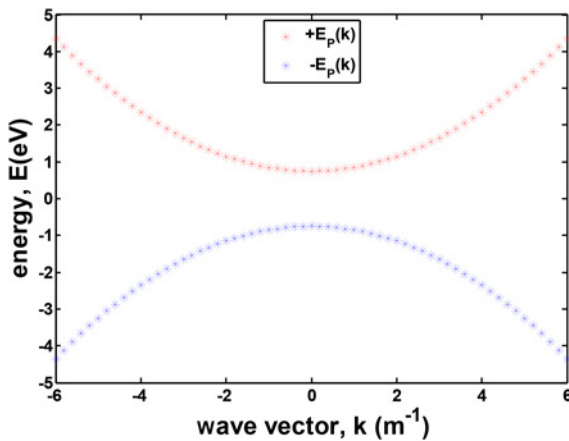
According to Fig. 2, energy dispersion of narrow width monolayer phosphorene shows non-zero energy bandgap and makes a distance between conduction and valance bands. The size of the gap depends on the number of layers; by increasing the number of layers the energy bandgap decreases [25–28]. Based on the one-dimensional behaviour of the phosphorene which has been reported by Li and Appelbaum [33], the density of states [34] as a fundamental parameter is defined which indicates available energy states with  $\Delta n$  quantum number in the length of  $L$  per energy  $\Delta E$  [34], and the effect of the electron spin is considered as well. By calculating the wave vector as  $k_x = (\sqrt{E - E_g}/\sqrt{A})$  and  $A = ((\hbar^2/2m_0) - (P_{x2}^2/E_{1x}) + (P_{x1}^2/E_g)) \times k_x^2$  the density of state is calculated as

$$\text{DOS}(E) = \frac{\Delta n}{\Delta E L} = \frac{(E - E_g)^{-1/2}}{4\pi\sqrt{A}} \quad (2)$$

Density of states is an essential parameter to calculate carrier concentration. The number of carriers (electrons) with energy,  $E$ , has been calculated to be  $\text{DOS}(E)f(E)dE$ . Therefore, carrier concentration in a band can be extracted by integrating the Fermi distribution function over the energy band [35]:

$$n = \int \text{DOS}(E)f(E)dE \quad (3)$$

where  $f(E) = (1/(1 + e^{(E-E_F)/k_B T}))$  is the Fermi-Dirac distribution function,  $k_B$  is the Boltzmann constant,  $E_F$  is the one-dimensional



**Fig. 2** Parabolic band structure of phosphorene in the vicinity of minimum energy ( $k = 0$ ) with conduction and valance bands separated by the bandgap  $E_g$

Fermi energy and  $T$  is the temperature [36]. The Maxwellian approximation  $\mathfrak{S}_i = e^\eta$  [37] is applied in the non-degenerate domain to evaluate the mobility of electrons. The position of Fermi level specifies the definition of non-degenerate and degenerate regimes. The non-degeneracy occurs when Fermi energy level located higher than  $3k_B T$  from either valence band or conduction band edge, or in other words when  $E - E_F \geq 3k_B T$ . Meanwhile, if Fermi level located inside conduction band (valence band) for electron (hole), or when  $E_F - E \leq 3k_B T$  degeneracy happens [38]. The carrier concentration can be calculated for an n-type black phosphorene as

$$n = \frac{\sqrt{k_B T}}{4\sqrt{A\pi}} \mathfrak{S}_{-(1/2)}(\eta) \quad (4)$$

where  $\mathfrak{S}_{-(1/2)}(\eta)$  is the Fermi-Dirac integral [39] of order  $-1/2$ .

By implementing achieved equations for density of states and carrier concentrations, the carrier velocity and mobility can be calculated which are required to model the electron relaxation time.

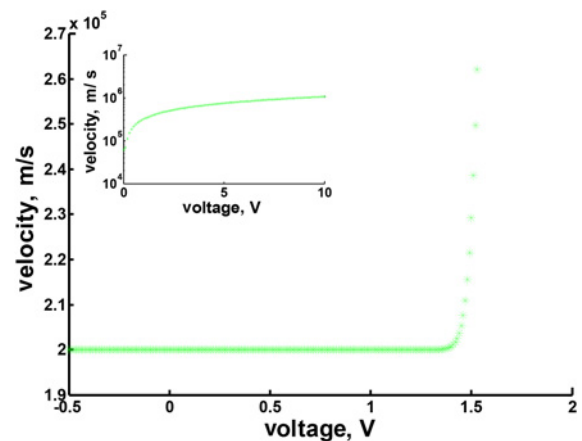
**2.1. Carrier velocity distribution:** In a semiconductor, free electrons can propagate along the crystal while colliding with atoms, the energy (kinetic energy) of which emerges from lattice vibrations. In equilibrium condition, electrons display random motions inside the crystal; while, on average electrons do not go anywhere. Usually, velocity depends on the carrier concentration and temperature. Therefore, the average velocity of the carriers can be obtained by

$$v_{av} = \frac{\int |v| \text{DOS}(E) f(E) dE}{n} \quad (5)$$

where  $|v| = ((2(E - E_g)/m))^{1/2}$  is the magnitude of velocity and  $n$  is the carrier density. In the absence of external field, electrons have completely random motion with ultimate velocity per electron equal to  $v_i$ . Therefore, by using the carrier-concentration relation and simplifying the final equation the intrinsic velocity for phosphorene can be achieved:

$$v_i = 16\pi^{3/2} \sqrt{\frac{2k_B T}{m}} \left( \frac{\mathfrak{S}_0(\eta)}{\mathfrak{S}_{-(1/2)}(\eta)} \right) \quad (6)$$

where  $\mathfrak{S}_0(\eta)$  is the is the Fermi-Dirac integral [39] of order zero and with  $\eta \simeq ((V_G - V_T)/k_B T/L)$  [40]. Fig. 3 indicates the carrier velocity versus potential difference between two contacts which is considered in the form of applied voltage. It can be seen that velocity increases with rising the voltage, especially for  $V \geq -1.2$  V. It is needed to be highlighted that the velocity is



**Fig. 3** Variation of electron velocity versus voltage

saturated for high applied voltages as shown in Fig. 3 in the logarithmic scale.

On the other hand, the dependency of carrier velocity on normalised Fermi energy is presented in Fig. 4. Based on the simulated results, it is shown that, as the value of  $\eta$  increases the velocity of electrons increases as well. The increment is strongly severe after  $\eta = -1.5$  where after this point the slope of the curve increases sharply. It is needed to be emphasised that in the logarithmic scale velocity indicates a saturation around  $10^6$  m/s which has been confirmed as a velocity limit in non-degenerate limit known as Fermi velocity [37].

Velocity is a function of  $\eta$ , so it is a function of  $T$  and consequently has an inverse relation with temperature [40]. As reported in [40], the normalised Fermi energy specifies inverse relation with temperature as shown in Fig. 5 which emphasises that carrier velocity decreases by increasing the temperature.

This is because of the increase in the number of collisions which occur for electrons due to the temperature rising. In a low carrier concentration, velocity is independent of carrier concentration and follows  $T^{1/2}$  behaviour. By increasing the carrier concentration to the degenerate regime, carrier velocity will be independent of temperature and strongly depends on carrier concentration. In the non-degenerate limit, the intrinsic velocity  $v_i$  saturates at thermal velocity  $V_{th}$ , as shown in the logarithmic scale of Figs. 3 and 4.

2.2. Mobility of electrons in black phosphorene: Without any external electric field, carriers in a semiconductor will have a random motion. Thereby, due to collisions of the carriers the

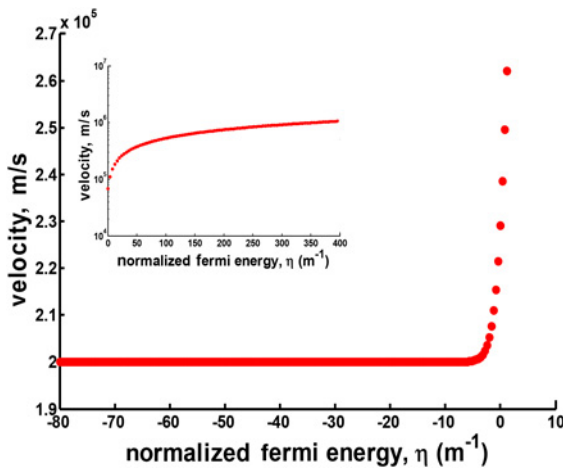


Fig. 4 Velocity dependency of electrons to the normalised Fermi energy

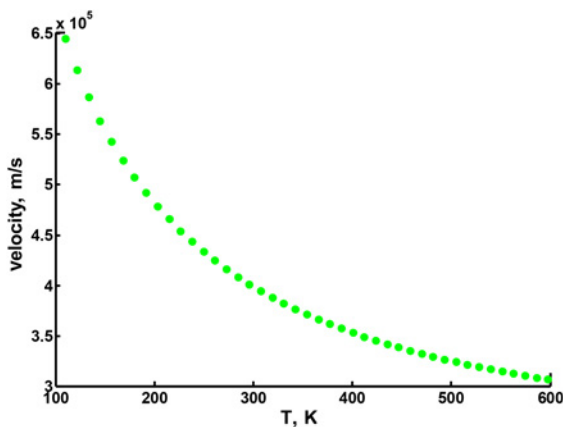


Fig. 5 Electron velocity variation versus temperature for monolayer phosphorene

energy and momentum of carriers will be randomised in order to remain in equilibrium state [41]. However, under non-zero applied electric field, the path of carriers between collisions will deviate leading to unidirectional motion and giving them drift velocity,  $v_d$ , in electric force,  $qE$  direction [41, 42], therefore the conduction carriers generate current. If the mean time between collisions is  $\tau_{sc}$ , the average velocity of carriers,  $v_{av}$ , for any value of field,  $E$  [42] then the effective mobility can be obtained which relates the velocity to this field [35]:

$$v_{av} = \mu E = \frac{q\tau_{sc}}{m^*} E \quad (7)$$

This indicates the relation of the carrier velocity with mobility,  $\mu$ , as well as electric field,  $E$ , the effective mass,  $m^*$ , and charge carrier,  $q$ . Where the carrier mobility  $\mu$  is the effective mobility which needs to be clarified that effective mobility can be written as

$$\mu = \mu_{0P} = \frac{\mu_0}{1 + t(V_G - V_T)} \quad (8)$$

When  $(V_G - V_T) = V_{GT} = 0 \rightarrow \mu_{0P} = \mu_0$  the effective mobility can be replaced by equilibrium mobility [where the applied voltage is zero  $V_{GT} = 0$  (this phenomenon is known as gate-field induced mobility degradation)]. On the other hand, it has been reported that the equilibrium mobility is under control of the thermal velocity ( $v_{th}$ ), because in the equilibrium condition applied voltage is zero therefore the temperature effect is more dominant [43]:

$$\mu_0 = \frac{q\tau}{m^*} = \frac{ql_0}{m^*v_{th}} \quad (9)$$

where  $l_0$  is the mean free path in the equilibrium condition which has been reported around 10 nm in the room temperature [44], and  $v_{th}$  is the thermal velocity. By bridging the thermal energy to the intrinsic velocity through the conservation of energy, the mobility for phosphorene is obtained,  $\mu_{0P}$  given by

$$\mu_{0P} = \frac{ql_0}{m^*v_{th}} \times v_i \quad (10)$$

By substituting intrinsic velocity relation from (6), the electron mobility for phosphorene is obtained as

$$\mu_{0P} = \frac{16ql_0\pi^2\sqrt{(2k_B T/m)}}{m^*v_{th}\sqrt{\pi}} \left( \frac{\mathfrak{Z}_0(\eta)}{\mathfrak{Z}_{-(1/2)}(\eta)} \right) \quad (11)$$

The variation of the electron mobility in terms of the normalised Fermi energy in non-degenerate domain is illustrated in Fig. 6. The normalised Fermi energy is commonly a function of temperature. Thus, in non-degenerate domains, mobility strongly depends on the temperature and rises with increasing the  $\eta$ .

It can be seen that mobility increases by increasing  $\eta$ , especially after  $\eta \simeq 1.5$  in which mobility dramatically increases for higher values of the normalised Fermi energy. Also, Fig. 7 shows the relationship between mobility and voltage. The variation of the mobility under applied voltage is severe after 1.5 V which highly increases by increasing voltage; it is because of increasing the velocity of the carriers under applied voltage. Since, the research on phosphorene is in initial steps, there are a few studies on phosphorene carrier statistics.

However, according to the theoretical and mathematical calculations, the presented models can be validated based on the trend of the figures clearly. The carrier mobility variations with respect to normalised Fermi energy, which is presented in Fig. 6, is comparable with the study of carrier mobility in graphene nanoribbon conducted by Amin *et al.* [45]. They showed that, mobility of carriers in graphene increases by increasing normalised Fermi energy [45]. Their findings are similar to the mobility of carriers in phosphorene

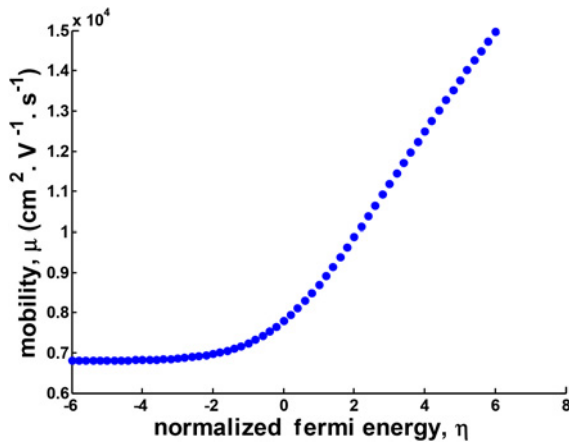


Fig. 6 Mobility dependency to the normalised Fermi energy in non-degenerate limit

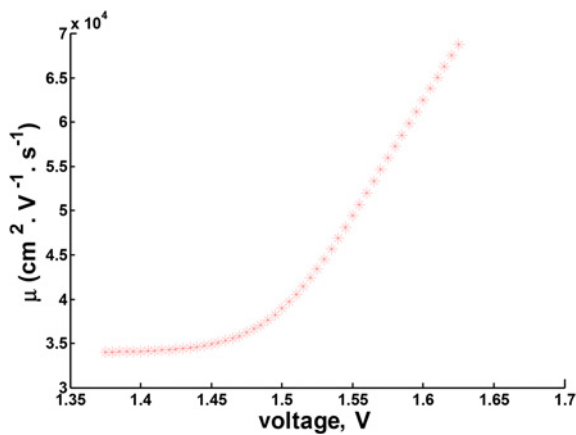


Fig. 7 Phosphorene carrier mobility in terms of voltage

as shown in Fig. 6. The mobility in the non-degenerate regime was found to decrease with increasing temperature, based on the simulation result as plotted in Fig. 8. The reduction occurs because of the higher rate of acoustic-phonon scatterings. By increasing temperature, concentration of the phonon in semiconductor increases and leads to increased scattering. Therefore, lattice scattering lowers the mobility of electrons more and more at higher temperatures. Upon reaching high temperatures, the calculated temperature value dependent on the charge mobility based on the presented model is found to become progressively weaker, as shown in Fig. 8.

The result of the mobility versus temperature for phosphorene can be compared with carrier mobility study in graphene by Amin *et al.* [45]. In the reported work, the mobility also decreases for higher values of the temperature in which the trend is quite similar to the mobility of carriers versus temperature in the phosphorene [45]. Furthermore, based on the first principle study by Liao *et al.* [44], phosphorene mobility was found to decrease by increasing the carrier concentrations for different temperatures. It was also demonstrated that the decrease of mobility is severe for lower temperatures. Their finding is consistent with our result in Fig. 8. Since as the temperature increases, the number of the carriers also increases, which induces decrease in the electron mobility.

On the other hand, based on (10), mobility has direct relation with velocity. Therefore, it can be concluded that the achieved results for the velocity variation in terms of temperature in Fig. 7 can be validated by the achieved results for the mobility. Our findings are also consistent with the results in the work by Liu *et al.* (2014), where they reported that mobility of the carriers in phosphorene was decreased by increasing the temperature [24].

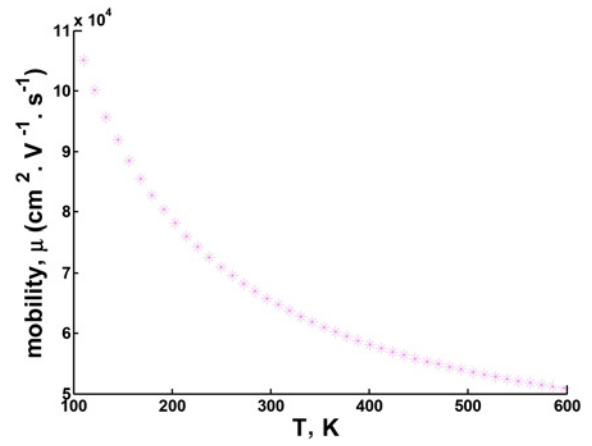


Fig. 8 Electron mobility changes versus temperature

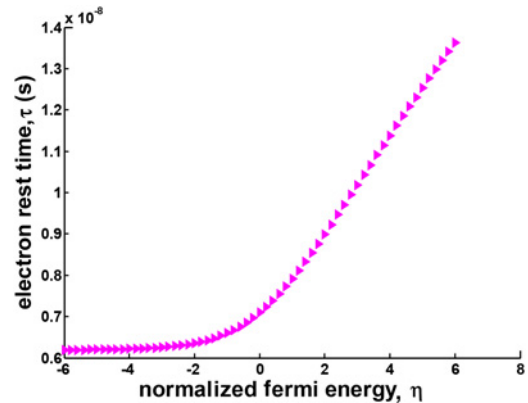


Fig. 9 Relaxation time of carriers as a function of normalised Fermi energy

**2.3. Relaxation time model:** The collision of electrons led to unexpected changes in the electron velocity with  $1/\tau$  probability per unit time. This indicates that the electron collision probability in any infinitesimal time interval of length  $dt$  is equal to  $dt/\tau$ . Therefore the time,  $\tau$ , is the average time between two successive scatterings of carriers. This is known as the relaxation time, and plays an important role in the metallic conduction theory. It is based on this assumption that a randomly selected electron at a given moment, on the average, before its net collision will travel for a time  $\tau$ .

Based on (7), the following expression is used to model the relaxation time of the electrons as a function of mobility (or normalised Fermi energy) in the monolayer phosphorene:

$$\tau_{sc} = \frac{\mu \times m^*}{q} \quad (12)$$

The electron relaxation time as a function of normalised Fermi energy is shown in Fig. 9. The electron relaxation time has increased with high slope for positive values of  $\eta$ . This indicates that carrier relaxation time is a function of temperature. In other words, as temperature decreases ( $\eta$  increases) carrier relaxation time increases. Since the lack of studies on the relaxation time of carriers in phosphorene, the obtained results for carrier relaxation versus normalised Fermi energy in Fig. 9 can be verified by the achieved results for the phosphorene carrier mobility. It was demonstrated that mobility of carriers increases by increasing the normalised Fermi energy. In other words, by increasing  $\eta$ , mobility and velocity of the carriers will be increased which leads to more collisions of carriers. The increment of collisions increases the relaxation time which is consistent with the trend of the results shown in Fig. 9.



The proposed models provide compact analytical relations which can be readily employed for investigation of basic parameters of phosphorene carrier statistics and their dependency on temperature in electronic devices.

**3. Conclusion:** The carrier relaxation time and carrier statistics of the monolayer phosphorene are analytically modelled for non-degenerate domain. The obtained results indicate that the carrier mobility and carrier velocity strongly depend on the temperature in non-degenerate regime in which mobility and velocity decrease by increasing the temperature from 100 to 300 K, which can be explained by the number of carriers resulting in a higher rate of collision between electrons. Nevertheless, for temperatures above 300 K, the mobility and velocity are less affected due to the acoustic phonon existence which is the dominant mobility limiting factor. Furthermore, it is found that the mobility highly increases for voltages above 1.5 V, which can be explained in the form of carrier concentration incremental effect. Also, the numerical simulation results for the velocity confirm same results. Finally, the carrier relaxation time as a function of normalised Fermi function is modelled. It can be seen that the relaxation time increases as the normalised Fermi energy rises (temperature decreases) which emphasises that by decreasing the temperature the number of collisions decreases.

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