CHAPTER 6

DIFFUSION THERMOPOWER IN MONOLAYER GRAPHENE

Part of the work presented in this chapter has appeared in

6.1 Introduction

The quest for achieving high figure of merit $ZT$ has made the physicists to search for new material systems which can be used to produce coolers for telecommunication lasers and high power solid state sources. The figure of merit $ZT$ is defined by $ZT = (S^2 \sigma / \kappa)T$, where $S$ is the thermopower, described by the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity. A high $ZT$ value is an indicative of efficient energy harvesting mechanism. Obtaining maximum value of $S$ is one of the ways to maximize $ZT$.

As discussed in Chapter 5, recently, there has been great deal of interest in electronic properties, both theoretically and experimentally, of 2D monolayer graphene (MLG), which is a monatomic layer of graphite [6.1-6.3]. Investigations of Novoselov et al [6.2] and Zhang et al [6.3] show in 2D monolayer graphene that the charge carriers are massless Dirac fermions with linear dispersion spectra due to the honey comb lattice structure of carbon atoms. The spectacular findings are universal minimum conductivity of the order of quantum conductance $\frac{e^2}{h}$, anomalous half integer quantum Hall effect, cyclotron mass $m_c$ of massless carriers in graphene described by $E = m_c v_F^2$ ($v_F$ is the Fermi velocity) and high mobility of samples which is basically shown to be independent of doping and temperature [6.2,6.3].

The theory of electron transport in MLG is discussed by different groups [6.4-6.7]. Qualitative agreement of calculations of Hwang et al [6.4] with the existing experimental data strongly indicates that the dominant carrier scattering mechanism is due to charged impurities located near the interface between the graphene and the substrate. Stauber et al [6.5] propose a new mechanism due to vacancies inducing midgap states accounting for experimental findings. Hwang and Das Sarma [6.7] have calculated the intrinsic temperature dependent mobility
limited only by the acoustic phonon scattering and mobility exceeding $10^5$ cm$^2$/Vs is found to be feasible. Measurements of Morozov et al [6.8] show that giant intrinsic carrier room temperature mobilities $2 \times 10^5$ cm$^2$/Vs, about hundred times more than the highest mobility observed so far in semiconductor heterojunctions, are achievable, if extrinsic disorder is eliminated. In view of high speed electrons, 2D graphene systems show potential to become high speed and high power transistors with the smallest size ever possible.

As discussed in Chapter 2, thermopower is another important transport property of any material for its applications in thermopower generation and thermoelectric coolers. It has two additive components: diffusion thermopower $S^d$ and phonon drag thermopower $S^p$. $S^p$ has been studied in monolayer graphene and is shown to be important for temperatures $T < 10$ K [6.9]. First phenomenological study of $S^d$ is given by Stauber et al [6.5] and Mott formula is given by Kubakaddi [6.9]. However, no detailed study of $S^d$ with respect to various scattering mechanisms, over a wide temperature range, existed at the time of our investigation. Since $S^d$ is a sensitive measure of energy dependence of the scattering mechanisms and electronic structure, we have undertaken study of $S^d$ to bring out the importance of various scattering mechanisms in limiting this property. It will provide valuable information about the possible scattering mechanism at a given temperature and helps to find out thermoelectric figure of merit for its possible applications in thermoelectric devices. In the present work, $S^d$ is studied due to charged impurity, vacancy and acoustic phonon scattering as a function of temperature $T$ and electron concentration $n_s$. This is the first quantitative study of $S^d$ in MLG reported by us in Ref. [6.10].
6.2 Analytical details

As explained in Chapter 2, thermopower $S$, is the electric field developed in a sample, in an open circuit condition, due to unit temperature gradient. As discussed in Chapter 5, monolayer graphene has linear relation between energy and momentum of the electrons and it is given by $E_k = \hbar v_F k$ (Eqn. 5.2.2.3) with $k$ being the 2D electron wave vector and $v_F$ being Fermi velocity. The density of states is given by $D(E_k) = (g_s \gamma_s \pi \hbar^2) E_k / v_F^2$ (Eqn. 5.2.2.5). Following the Boltzmann transport formalism described in Ref. [6.11], which is applicable to two-dimensional electron gas (2DEG), we obtain the expression for $S^d$ in monolayer graphene with $\nabla T$ in its plane. Using the above mentioned dispersion relation and density of states, the expression for $S^d$ becomes,

$$S^d = (1/eT) \left[ -E_F + \left( \frac{E_k \tau(E_k)}{\tau(E_k)} \right) \right], \quad (6.2.1)$$

where $E_F$ is the Fermi energy, $e$ is the electron charge, $f^0$ is equilibrium Fermi-Dirac distribution function and

$$\langle \tau(E_k) \rangle = \int E_k \tau(-df^0/dE_k) dE_k / \int E_k (-df^0/dE_k) dE_k \quad (6.2.2)$$

is the average momentum relaxation time of electrons. Interestingly, although density of states in MLG is energy dependent, the equation for average relaxation time is found to be same as that of conventional 2DEG (Eqn. 2.2.2).

In the complete degenerate limit Eqn.(6.2.1) leads to the well known Mott formula and it is given by

$$S^d = -\frac{\pi^2 k_B^2 T}{3e} \left[ \frac{d\ln\sigma(E_k)}{dE_k} \right]_{E_k = E_F} \quad (6.2.3)$$

With the electrical conductivity $\sigma(E_k) = e^2 v_F^2 D(E_k) \tau(E_k)/2$ and the relaxation time $\tau(E_k)$ expressed as $\tau(E_k) \sim (E_k)^\gamma$, the equation of $S^d$ is [6.9].
\[ S^d = \frac{\pi^2 k_B^2 T}{3eE_F} (p + 1), \]  

(6.2.4)

with \( p \) being the scattering parameter. This is also same as found in conventional 2DEG (Eqn. 2.2.4).

6.3 Relaxation time

The possible scattering mechanisms, we considered, that limit the mobility in graphene are discussed in detail and given in Chapter 5. They are, scattering due to Coulomb potential (charged impurities), vacancies (midgap states) and acoustic phonons. We use the corresponding relaxation times given in Chapter 5 for the calculation of \( S^d \).

Relaxation time due to charged impurities is given by Eqn. (5.3.1.3) and relaxation time in the case of scattering due to vacancies is given by Eqn. (5.3.2.2). From these Eqns. we observe that, largely \( \tau (\varepsilon_k) \sim \varepsilon_k \) for both impurity and vacancy scattering with an additional weak logarithmic dependence in the latter case.

The relaxation time due to acoustic phonon scattering in the equipartition regime (phonon energy \( \hbar \omega_q \ll k_B T \)) is given by Eqn. (5.3.6.4). It gives \( \tau (\varepsilon_k) \sim 1/\varepsilon_k \) energy dependence.

The resultant relaxation time, which is obtained by using Mattheissen’s rule

\[ (1/\tau) = (1/\tau_{\text{imp}}) + (1/\tau_{\text{vac}}) + (1/\tau_{\text{acdp}}), \]  

(6.3.5)

will be used to calculate \( S^d \) due to all the mechanisms combined.

6.4 Results and discussion

The material parameters used for graphene are: \( v_s = 2.0 \times 10^4 \text{ m/s} \), \( v_F = 9.8 \times 10^5 \text{ m/s} \) and \( \Xi = 19 \text{ eV} \) [6.7]. We take \( n_i^e = n_i = 2.0 \times 10^{14} \text{ m}^{-2} \), the commonly used values
in the literature for illustration. First we present $S^d$ and mobility $\mu$ calculation as a function of $T$ in the range 0-300K for $n_s = 1 \times 10^{16} \text{m}^{-2}$.

Figure 1: Diffusion thermopower $S^d$ as function of temperature $T$ for $n_s = 1 \times 10^{16} \text{m}^{-2}$. Inset: Mobility $\mu$ vs $T$. Curves shown in both the figures are for charged impurity (dashed), vacancies (dash-dotted), acoustic phonons (dotted) and combined due to all the scattering mechanisms (continuous).

Fig. 1 shows $S^d$ vs $T$ due to each of the mechanisms and all the mechanisms combined. Inset shows mobility $\mu$ vs $T$. $\mu$ is obtained from electrical conductivity $\sigma = n_s e \mu$, where $\sigma = e^2 v_F^2 <D(E_k)r(E_k)>/2$. For the chosen parameters, the mobility is largely limited by vacancies (dash-dotted curve). The dominance of the scattering mechanism can be seen from the curves where the resultant mobility (continuous curve), due to all the scattering mechanisms, is close to the mobility due to vacancy scattering (dash-dotted). This is in agreement with the mobility calculations in Ref.
[6.5]. However, the work of Ref. [6.4] indicates the dominance of impurity scattering. Basically, we note that relative contribution of these mechanisms to $\mu$ is decided by the concentration of vacancies and impurities.

We observe that $S^d$ due to scattering by charged impurity (dashed) and vacancies (dash-dotted curve) is giving a linear $T$ dependence over the entire temperature range but with different slopes. The slopes and magnitudes in a degenerate electron gas are largely determined by the energy dependence of their relaxation times. The $S^d$ due to acoustic phonons (dotted curve) deviates from the linear behavior. $S^d$ due to vacancy and impurity scattering are nearly of the same order of magnitude as found for 2DEG in GaAs heterojunctions and Si-MOSFET [6.12, 6.13]. At 300 K, we observe that $S^d$ due to charged impurity is about 1.3 (20) times that due to vacancy (acoustic phonon) scattering. However, it is to be noted that, the dominance of a scattering mechanism in limiting $S^d$ can be determined by comparing $S^d$ due to overall $\tau$ (i.e. continuous curve) with those due to individual mechanisms. In the present calculation, $S^d$ due to combined $\tau$ is close to $S^d$ due to vacancies indicating the dominance of this scattering mechanism. And it is consistent with observation in mobility. $S^d$ due to acoustic phonons is showing almost negligible contribution. A rough estimation of this can be seen from the Mott formula which shows $S^d=0$ with $p=-1$ for acoustic phonon scattering. However, in the samples free from extrinsic disorders, at higher $T$, transport is mainly limited by phonon scattering [6.7]. Under such circumstances observed $S^d$ may be very small.

In Fig.2, we have presented calculations of total (due to all the scattering mechanisms combined) $S^d$ vs $T$ for three different concentrations ($n_s=1$, 5, $10^{16}$ m$^{-2}$). The total $S^d$ decreases, as expected, with increase in $n_s$. Comparing to the total
$S^d$ for $n_s=1\times10^{16}\text{m}^{-2}$ (continuous line) $S^d$ decreases nearly 1.5 times for $n_s=5\times10^{16}\text{m}^{-2}$ (dashed line) and nearly 2 times for $n_s=10\times10^{16}\text{m}^{-2}$ (dotted line).

Figure 2: $S^d$ due to all the mechanisms combined vs $T$ for $n_s=1, 5, 10\times10^{16}\text{m}^{-2}$. The curves shown are corresponding to $n_s=1\times10^{16}\text{m}^{-2}$ (continuous line), $n_s=5\times10^{16}\text{m}^{-2}$ (dashed line) and $n_s=10\times10^{16}\text{m}^{-2}$ (dotted line).

$S^d$ is also studied as a function of $n_s$ (1-$10\times10^{16}\text{m}^{-2}$) at $T=300\text{K}$ and it is shown in Fig. 3. Inset shows $\mu$ vs $n_s$. $S^d$ decreases monotonically with the increasing $n_s$. Again, $S^d$ due to acoustic phonon scattering is found to be negligible, even at room temperature. The $S^d$ due to vacancy and impurity scattering are equally significant, as can be seen by the continuous curve due to combined $\tau$, over the range of $n_s$ considered. It is to be noted that, at very low $T$, $S^d$ changes sign in Si-MOSFET when $n_s$ is varied [6.12]. It is basically decided by the value of $p$ and dominant scattering mechanism. At very low $T$, we find $S^d \sim n_s^{-1/2}$ where as in conventional
2DEG $S^d \sim n_s^{-1}$. This difference may be attributed to the linear dispersion relation between electron energy and its wave vector in graphene. The variation of $S^d$ with $n_s$ can be easily verified in graphene experimentally as it is possible to vary $n_s$ by gate voltage [6.1]. From the inset it can be observed that, total mobility (due to all the scattering mechanisms) decreases with increase in $n_s$. Here we point out that, for about $n_s < 5 \times 10^{16}$ m$^{-2}$, scattering due to vacancies are dominant, where as for about $n_s > 5 \times 10^{16}$ m$^{-2}$ acoustic phonons are dominant and limit mobility.

![Graph showing $S^d$ vs $n_s$ at $T=300$K and $n$ vs $n_s$. Curves shown in both the figures are for charged impurity (dashed), vacancies (dash-dotted), acoustic phonons (dotted) and combined due to all the scattering mechanisms (continuous).](image)

**Figure 3**: $S^d$ as function of $n_s$ at $T=300$K. Inset: $\mu$ vs $n_s$. Curves shown in both the figures are for charged impurity (dashed), vacancies (dash-dotted), acoustic phonons (dotted) and combined due to all the scattering mechanisms (continuous).

In Fig. 4, we have also calculated total $S^d$ vs $n_s$ for three different $T = 100$K (dotted line), 200K (dashed line) and 300K (Solid line). It is noted that, for
$n_e=1 \times 10^{16} \text{m}^{-2}$ total $S^d$ is low for $T=100\text{K}$ and increases as $T$ increases. This is due to linear dependence of $S^d$ with $T$.

Figure 4: Total $S^d$ vs $n_e$ for different temperatures. The curves shown are for $T=100\text{K}$ (dotted line), 200K (dashed line) and 300K (Solid line).

It is worth noting that due to electron-hole symmetry (i.e. with the Fermi energy $E_F=0$) thermopower vanishes in single wall carbon nanotube [6.14, 6.15] and graphene [6.16]. However, large thermopower can be obtained by breaking the electron-hole symmetry. Defect states do break symmetry and may lead to large value of the thermopower [6.15, 6.16]. In our calculation, with $E_F>0$, contribution due to only electrons is considered.

Recently, after our work has been carried out, thermopower has been studied experimentally [6.17-6.19] and theoretically [6.20-6.23] by different groups. Zuev et al [6.18] observed experimentally $S \sim 50 \mu \text{V/K}$ at $T=300$ K for $n_e=2 \times 10^{16} \text{m}^{-2}$, which
is closer to our calculated value of $S^d \sim 65 \mu V/K$ for the same $T$ and $n_s$. Hwang et al [6.20] calculated $S^d$ and found that, scattering by charged impurity gives reasonable agreement with the measured thermopower [6.17-6.19]. The effects of scattering due to short-range disorder and phonons are found to be negligible in experimental temperature range $T < 300K$. The shortcoming of the Mott’s formula at high temperature range has also been discussed. Bao et al [6.22] have made a quantitative study of phonon drag and diffusion thermopower. It has been shown that $S^d$ dominates over $S^d$ for $T < 10 K$, consistent with the findings of Kubakaddi [6.9]. $S^d$ calculations of Bao et al, employing the technique of balance equation approach, include scattering due to impurity and phonons to account for the observed thermopower. Later calculations of $S^d$ are carried out, employing the approach given by us, including scattering due to surface roughness and optical phonons in addition to the scattering due to charged impurities, vacancy and acoustic phonons (mechanisms considered by us) [6.23]. Calculations by these authors support our predictions that $S^d$ due to vacancy and charged impurity scattering mechanisms are much larger. $S^d$ due to acoustic phonons, optical phonons and surface roughness is shown to be negligible.

In conclusion, diffusion thermopower $S^d$ is studied as sensitive probe of scattering mechanism in monolayer graphene. It is calculated for scattering due charged impurities, vacancies (midgap states) and acoustic phonons as function of temperature $T$ and electron concentration $n_s$. Relative dominance of the scattering mechanisms is discussed. Recent experimental and theoretical observations support our theoretical predictions. The calculation of $S^d$ made in the present work is a significant contribution in the study diffusion thermopower of monolayer graphene.
References:


