2.1 Introduction

Thermopower $S$, one of the important transport properties, finds applications in thermoelectric power generation. Industrial applications of thermoelectric materials have generated increased activity in this field by demanding higher performance near room temperature. A high value of thermoelectric figure of merit $ZT (~S^2)$ is an indicative of efficient thermal energy harvesting mechanism which finds applications in small-scale localized cooling in computers, infrared detectors, electronics, optoelectronics and many other. It is sensitive to the scattering mechanisms and providing information of electronic structure and physical processes involved in the transport phenomena. Thus, the potential payoff for the development of thermoelectric devices is great, and the requirement for compounds with properties optimized over wide temperature range has led to a much-expanded interest in new thermoelectric materials [2.1-2.3]. The search for thermoelectric materials with a larger thermoelectric figure of merit has become a topic of extensive experimental and theoretical work, and motivated researchers to study thermopower extensively in conventional low dimensional semiconductor structures [2.4, 2.5].

The thermopower (Seebeck coefficient) of a conducting material is a measure of the magnitude of an induced thermoelectric voltage $\Delta V$ in response to a temperature difference $\Delta T$ across that material in open circuit condition, which opposes the motion of the carriers due to induced voltage. It is defined by

$$E = S \nabla T$$

(2.1.1)

where $E$ is the electric field produced by the temperature gradient $\nabla T$.

Figure: 2.1. A schematic illustration of the Seebeck effect of a material in which a voltage difference ($\Delta V$) is generated due to the temperature difference ($\Delta T$) between the ends.

There are two additive independent contributions to $S$: diffusion thermopower, $S^d$ and phonon-drag thermopower $S^p$, $S = S^p + S^d$. The contribution $S^d$ arises from the diffusive motion of the carriers in the temperature gradient and it is sensitive to energy dependence of the scattering mechanisms. Moreover, it is complimentary to
the electrical conductivity. $S^g$ arises due to phonon wind, set up in a temperature gradient, which drags and transfers its momentum to electrons because of the electron-phonon coupling. The magnitude of $S^g$ depends on the strength of the interaction between the electrons and phonons. Also, the phonon-electron relaxation time should be shorter than phonon-phonon relaxation time. That is because to enhance thermoelectric voltage phonons should preferentially lose their momentum to the electrons rather than to other phonons.

Both $S^d$ and $S^g$ are not separable experimentally [2.5, 2.6]. The measured thermopower in the temperature range about 1-10 K was found to be subsequently larger than the magnitude of $S^d$. The temperature dependence of $S^d$ is largely linear. Generally, $S^g$ is dominant in the low temperature (< 15 K) regime.

2.2 General formalism of thermopower in graphene

We consider graphene, a strictly two-dimensional (2D) conducting medium, under the influence of a weak static electric field $E$ and temperature gradient $\nabla T$ in $xy$-plane. Electrons are ideally 2D in nature with chiral character as described in Chapter 1. A macroscopic electric current density $J$ and heat current density $U$ are produced in this medium. These are obtained by using the steady state solution for electron distribution function $f_k$ obtained from Boltzmann transport equation technique, in the relaxation time approximation, in the presence of $E$ and $\nabla T$ [2.7, 2.8]. The equations for $J$ and $U$ are, respectively, given by

$$J = -\frac{1}{4\pi^2} g_x g_y |e| \int f_k v_k d^2k$$

$$= e^2 K_0 \cdot E + \frac{|e|}{T} K_1 \cdot (-\nabla T), \quad (2.2.1)$$

and

$$U = \frac{g_x g_y}{4\pi^2} \int f_k (E_k - E_f) v_k d^2k$$

$$= |e| \cdot K_1 \cdot E + \frac{1}{T} K_2 \cdot (-\nabla T), \quad (2.2.2)$$

where

$$K_n = \frac{g_x g_y}{4\pi^2} \int \tau(E_k) v_k v_k (E_k - E_f)^n (\partial f_k^0 / \partial E_k) d^2k. \quad (2.2.3)$$
Here, \( f_k^0 = \frac{\exp(E_k - E_f)}{k_B T + 1} \) is the Fermi-Dirac distribution, \( E_f \) is the Fermi energy, \( \tau(E_k) \) is the electron momentum relaxation time and \( v_k \) is electron group velocity.

The above equations for \( J \) and \( U \) can be expressed in terms of the transport coefficients \[2.7-2.9\]

\[ J = \sigma E + L \nabla T \quad (2.2.4) \]

and

\[ U = M E + N \nabla T, \quad (2.2.5) \]

where \( \sigma \) is the electrical conductivity, coefficients \( L, M \) and \( N \) are in general tensors and are related to \( K_n \)'s. These coefficients are not measured experimentally. In order to relate to the experimentally measured quantities we write the above equations in the form

\[ E = \rho J + S \nabla T \quad (2.2.6) \]

and

\[ U = \Pi J - \kappa \nabla T \quad (2.2.7) \]

In the above expression \( \rho = \sigma^{-1} \), \( S = -L/\sigma \), \( \Pi = M/\sigma \) and \( \kappa = [(M\sigma^{-1}L) - N] \) are, respectively, electrical resistivity, thermopower, Peltier coefficient and thermal conductivity. Peltier coefficient and thermopower are related by \[2.8\]

\[ S = \Pi / T = M/\sigma T \quad (2.2.8) \]

which is one of the Kelvin relations of thermo-electricity, and a special case of Onsager relations of thermodynamics of irreversible process.

2.2.1 Diffusion thermopower in graphene

Under open circuit condition, setting diffusion current density \( J^d = 0 \), the expression for diffusion thermopower is obtained using Eqns (2.2.1) and (2.2.3). It is given by

\[ S^d = -L^d / \sigma = (1/|e|T)K_1 K_0^{-1} \quad (2.2.9) \]

Eqn. (2.2.9) can also be written, using Eqn. (2.2.3), as

\[ S^d = -(1/|e|T)[\langle \tau(E_k)E_k \rangle / \langle \tau(E_k) \rangle - E_f ], \quad (2.2.10) \]

where
Basic formalism of thermopower in graphene

\[
\langle x \rangle = \left[ x E_k (\partial f_k^0 / \partial E_k) dE_k \right] / \left[ \int E_k (\partial f_k^0 / \partial E_k) dE_k \right]
\]

(2.2.11)
is the average over \( f_k^0 \). In the complete degenerate case, i.e. for large electron concentration and low temperature, Eqn. (2.2.9) gives the Mott formula

\[
S^d = -\frac{\pi^2 k_B^2 T}{3 |e|} \left[ \frac{d \sigma(E_k)}{dE_k} \right]_{E_k = E_f}
\]

(2.2.12)

where \( \sigma(E_k) \) is the energy dependent electrical conductivity.

### 2.2.2 Phonon-drug thermopower in graphene

In the following, to obtain \( S^g \), we consider a graphene system in which both electrons and phonons are two-dimensional.

There are two equivalent approaches to \( S^g \). In the temperature gradient \( \nabla T \) along \( xy \)-plane (which produces a phonon flow along the direction of the gradient from hot to cold end) the non-equilibrium phonons transfer part of their momentum to electrons via the electron-phonon interaction producing phonon-drug current density

\[
J^g = L^g \nabla T.
\]

(2.2.13)

In the open circuit condition an electric field \( \mathbf{E} = S^g \mathbf{\nabla} T \) is set up to stop \( J^g \). \( S^g \) is readily obtained by

\[
S^g = -L^g / \sigma.
\]

(2.2.14)

This method is called Q-approach [2.10].

In the second one, the electrons are accelerated isothermally in the presence of an electric field \( \mathbf{E} \) and impart some of their momentum to phonons due to electron-phonon coupling. Then from the phonon heat current density

\[
U^g = M^g \mathbf{E} = M^g J^g / \sigma
\]

(2.2.15)

and the Onsager’s relation \( S = \Pi / T \), with \( \Pi = U^g / J^g \), gives

\[
S^g = M^g / \sigma T.
\]

(2.2.16)

This method of \( S^g \) calculation is called \( \Pi \)-approach [2.11].

The first approach used here is conceptually simpler and it has been widely used for the study of \( S^g \) [2.5, 2.6, 2.10, 2.12]. Cantrell and Butcher have developed the theory of \( S^g \) for a system of quasi-2D electrons interacting with 3D phonons in semiconductor heterostructures [2.12]. We adopt the same method to obtain \( S^g \) in
graphene with suitable modifications that the 2D electrons with chiral character are assumed to interact with the 2D phonons.

In presence of $\nabla T$, the electric current density $\mathbf{J}$ is expressed in terms of the steady state electron distribution function $f_k$ by

$$
\mathbf{J} = -\frac{g_s g_v |e|}{A} \sum_k f_k \mathbf{v}_k .
$$

(2.2.17)

In a thermal gradient $\nabla T$, both electrons and phonons are in non-equilibrium. In this case the steady state $f_k$ is determined by solving the coupled Boltzmann transport equations for electrons and phonons [2.6, 2.12]. The steady state Boltzmann equation for electrons is given by

$$
\mathbf{v}_k \cdot \nabla_r f_k - (|e|/h) \mathbf{E} \cdot \nabla_k f_k = (\partial f_k / \partial t)_{\text{coll}},
$$

(2.2.18)

The first and the second terms are, respectively, the rate of change of $f_k$ due to the electron diffusion along the thermal gradient and electron acceleration by external field. The collision term is written as sum of the contribution from elastic collisions and phonons

$$
(\partial f_k / \partial t)_{\text{coll}} = -[(f_k - f_k^0) / \tau_{es}(E_k)] + (\partial f_k / \partial t)^{a}_{ep} + (\partial f_k / \partial t)^{e}_{ep},
$$

(2.2.19)

where the first contribution refers to the electron elastic scattering with relaxation time $\tau_{es}(E_k)$ and the other two terms denote the electron scattering by phonons. The superscripts $a$ and $e$ refer to the phonon absorption and emission, respectively. The collision term due to electron-phonon scattering is given by

$$
\left\{ \frac{\partial f_k}{\partial t} \right\}_{\text{ep}}^{a(e)} = \sum_{k',q,s} [f_{k'} (1 - f_{k'}) P_{q,s}^{a(e)}(k',k) - f_k (1 - f_k') P_{q,s}^{a(e)}(k,k')] ,
$$

(2.2.20)

where $P_{q,s}^{a(e)}(k,k')$ is the intrinsic rate of electron transition from a state $k$ to a state $k'$ by absorbing (emitting) one acoustic phonon. The transition rates are obtained by Fermi golden rule

$$
P_{q,s}^{a} = (2\pi/h)N_{q,s} |M(k,k')|^2 \delta(E_{k'} - E_k - \hbar \omega_{q,s}) \delta_{k',k+q},
$$

(2.2.21)

where $\delta(E_{k'} - E_k - \hbar \omega_{q,s})$ is the Dirac $\delta$-function that expresses energy conservation, $\delta_{k',k+q}$ is the Kronecker $\delta$-symbol that secures momentum conservation in $xy$-plane, $\hbar \omega_{q,s}$ is the energy of acoustic phonons in mode $s$, $q = (q_x, q_y)$ is the 2D phonon wave vector.
\(N_{q,s}\), the phonon distribution, is determined by the steady-state Boltzmann equation for phonons in the relaxation time approximation

\[\nabla_r N_{q,s} = [(N_{q,s} - N^0_{q,s})/\tau_p(q,s)] + (\partial N_{q,s}/\partial t)_p,\]  \tag{2.22}

where \(\nu_p(q,s)\) is the 2D phonon group velocity. The first term on the right-hand side is due to phonon collision with the boundaries and the lattice imperfections characterized by the relaxation time \(\tau_p(q,s)\), and

\[N^0_{q,s} = 1/[\exp(h\omega_{q,s}/k_BT) - 1]\]  \tag{2.23}

is the Bose distribution function. The rate of change of phonon distribution due to electron scattering is given by

\[(\partial N_{q,s}/\partial t)_p = g_v g_s \sum_{k,k'} [f_{k'}(1-f_{k'})P^d_{q,s}(k,k') - f_k(1-f_{k'})P^a_{q,s}(k,k')].\]  \tag{2.24}

The electron and the phonon distribution functions are coupled due to the simultaneous occurrence of \(f_k\) and \(N_{q,s}\) in Eqns. (2.2.20) and (2.2.24). Assuming that the thermal gradient and electric field are sufficiently weak, the electron and the phonon distribution functions are linearized by writing \(f_k = f^0_k + f^1_k\) and \(N_{q,s} = N^0_{q,s} + N^1_{q,s}\), where \(f^1_k\) is associated with \(\nabla T\) and \(E\) and \(N^1_{q,s}\) to \(\nabla T\). Substituting these in the Eqn. (2.2.17) gives \(J^e = L^g\nabla T\). Then, \(S^g = (-L^g/\sigma)\) is given by

\[S^g = \frac{g_s g_v |e|}{2A\sigma k_BT^2} \sum_{k,k'} \sum_{q,s} h\omega_{q,s} \tau_p(q,s) \tau_{es}(E_k) v_k \cdot \nu_p(q,s)(\Gamma_{k,k'} - \Gamma_{k,k'}).\]  \tag{2.25}

Rearranging Eqn. (2.2.25) by interchanging \(k\) and \(k'\) in the second term of the sum, we obtain

\[S^g = \frac{g_s g_v |e|}{2A\sigma k_BT^2} \sum_{k,k'} \sum_{q,s} h\omega_{q,s} \tau_p(q,s) \Gamma_{k,k'} v_p(q,s) \{\tau_{es}(E_k) v_k - \tau_{es}(E_k) v_{k'}\}.\]  \tag{2.26}

In the above equation

\[\Gamma_{k,k'} = f^0_k(1-f^0_k)P^a_{q,s}(k',k)\]  \tag{2.27}

with
Using the above basic formalism, we investigate (i) the diffusion thermopower in bilayer graphene in Chapter 3 and (ii) the phonon-drag thermopower in a bilayer graphene and an armchair graphene nanoribbon, respectively, in Chapters 4 and 5.
Reference


