Spin caloritronics in magnetic/non-magnetic nanostructures and graphene field effect devices
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DOI:
10.1038/nphys2743

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2015

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Dejene, F. (2015). Spin caloritronics in magnetic/non-magnetic nanostructures and graphene field effect devices [Groningen]: University of Groningen DOI: 10.1038/nphys2743

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Chapter 7

Thermoelectric effects in graphene field effect transistors

Abstract

In this chapter we present the electrical measurements of the Seebeck and Peltier effects in a single-layer graphene at room temperature. By measuring both the Seebeck and Peltier coefficients in a single device consisting of a microfabricated Joule heater, to create temperature gradients, and a nanoscale thermocouple, to measure local (interfacial) temperature changes, we also test the Thomson-Onsager reciprocity relation which thus far remained unexplored for graphene. In addition to showing the possibility of tunable thermoelectric conversion or refrigeration applications entirely based on graphene, thermoelectric measurements serve as a complimentary tool to gain a deeper understanding of electrical transport mechanisms such as hot electron relaxation pathways.

7.1 Seebeck and Peltier effects in graphene

The Seebeck and Peltier effects are two common thermoelectric phenomena that are widely used in thermometry and refrigeration applications. The Seebeck effect, the generation of a voltage $\Delta V$ due to a temperature difference $\Delta T$, is quantified by the material dependent Seebeck coefficient $S = -\Delta V/\Delta T$ that simply relates the amount of thermal energy carried by an electron for a unit temperature increase. The reverse process known as the Peltier effect, the generation of heat current $Q$ at an interface between two dissimilar materials when passing a charge current $I$, is set by the Peltier coefficient $\Pi = Q/I$ that specifies the amount of thermal energy carried by charge carriers. These two thermoelectric transport coefficients are linked to each other by the Thomson-Onsager reciprocity relation (ORR) as $\Pi = S T_0$, where $T_0$ is temperature (see section 2.1 for detail). Because these thermoelectric effects arise from the energy dependence of the electrical conductivity $\sigma$, they are often used as sensitive probes of small variations in the transport properties of a material, giving a better understanding of the energy dependent transport in near-equilibrium phenomena [1, 2]. In this regard, probing electronic correlations [3], mapping local density of state variations around the Fermi energy [4], exploring...
the electronic structure of molecular junctions [5], and imaging structural defects in epitaxial graphene [6] are few examples.

Recently, two dimensional materials such as MoS$_2$ [7, 8], black-phosphorus [9] and graphene are shown to exhibit very large and gate-tunable $S$ values. Several reports on the thermopower measurement of a single [3, 10–12] and bilayer graphene [13, 14] demonstrated tunable $S$ from large positive (in the p-doped hole regime) to large negative (in the n-doped electron regime) at room temperature. The linear scaling with temperature and thermal Hall response (Nernst effect) to a magnetic field [11] has also been shown giving additional insight in the transport properties of graphene.

Although a large and tunable $\Pi$ is also expected from the ORR relation, its nature in graphene remains largely unexplored due to the difficulty of measuring the often-small Peltier effect. Because the Peltier effect occurs at a metal/graphene interface and is often very small compared to Joule heating, its detection requires a sensitive thermometry architecture that is capable of measuring milikelvin temperature changes. Earlier reports on the electrical measurement of the thermopower in graphene utilized resistive thermometry technique [10, 12]. This technique, however is not suitable for the study of the Peltier effect due to its low sensitivity and very small spatial resolution that is limited only to micrometer sized regions. Furthermore, depending on the width of the used heater and graphene flake, this technique might over (under)-estimate the temperature gradient (Seebeck coefficient) [12]. Thus far only the work by Grosse et al.,[15] could show Peltier heating and current crowding at metal/graphene interfaces, but was only in the p-doped regime with a strongly limited gate voltage tunability. Further experiments that explore the tunable thermal properties of graphene are therefore highly required for the complete understanding and realization of Peltier cooling in graphene at a device level.

In this chapter, using a thermocouple based thermometry technique that can sensitively probe local temperature changes close to a Au/graphene interface, we directly measure both the Peltier and Seebeck effects in a single device and test the validity of the Thomson-Onsager reciprocity relation. The use of the NiCu-Au thermocouple close to the Au/graphene interface allows direct access to the interface nature of the Peltier effect, that can not otherwise be probed by the resistive thermometry technique. Further, in addition to providing a larger sensitivity ($\sim -10 \, \mu V/K$) for accurate measurement of small temperature changes ($\sim 1 \, mK$), its placement outside the current path allows us to exclude any charge related effects.
7.2 Sample preparation and measurement technique

The graphene flakes studied here were exfoliated onto a 500 nm thick SiO$_2$ substrate on a heavily doped Si substrate that serves as a gate for tuning the charge carrier...
density in the graphene flake. After the selection of a suitable graphene flake and identification of the number of layers using atomic force and optical microscopy, the Ti/Au (5/35 nm) electrodes were fabricated using standard e-beam lithography, e-beam evaporation and lift-off technique. The 40 nm thick constantan (Ni$_{45}$Cu$_{55}$), which is used as one arm of the thermocouple, was sputter deposited at an Ar pressure of $3 \times 10^{-3}$ mbar after a short Ar-ion cleaning (for 20 sec at a beam voltage of 500 V and beam current of 14 mA) of the Au electrodes to ensure good electrical and thermal contact. We performed three types of measurements—four-probe electrical conductivity, thermopower and Peltier measurements. The schematic configuration of the thermopower and Peltier measurements are shown in Figs. 7.1(a) & (b), respectively. The conductivity measurements are used to characterize the quality of the graphene flake as well as extract the mobility of charge carriers in graphene. In the Seebeck measurement [see Fig. 7.1(a)], an electrically isolated Joule heater is used to generate an in-plane temperature difference $\Delta T$ along the graphene flake and the open circuit thermovoltage $\Delta V$ is measured using the Au electrodes on the graphene flake [3, 10, 13, 16]. The thermovoltage response appearing as a second harmonic signal is measured using a lock-in amplifier (see Appendix B for the details). In the Peltier measurement [see Fig. 7.1(b)], a charge current is sent through the graphene–Au interface and the resulting temperature change is probed using the local Ni$_{45}$Cu$_{55}$-Au thermocouples.

All measurements were performed in vacuum at room-temperature using AC lock-in measurement technique to distinguish the Peltier heating/cooling ($\propto I$) from higher order contributions such as Joule heating ($\propto I^2$). Note that the experimentally measured thermovoltage responses are in the order of a few mV and hence we took care that any capacitive or inductive contributions to the signal are excluded by carefully checking the frequency dependence of the measured signals. In addition, common mode signals that are not differential in origin were subtracted from the measurements by performing two measurement with reversed voltage probes and averaging them to obtain the common mode contributions.

### 7.3 Finite element simulation of thermoelectric effects

Before we present the main results of our measurement here we describe the three dimensional finite element model (3D-FEM) which is constructed using the software COMSOL Multiphysics®. In this model the charge ($\vec{J}$) and heat ($\vec{Q}$) current densities are related to the respective voltage and temperature gradients as

$$
\begin{pmatrix}
\vec{J} \\
\vec{Q}
\end{pmatrix} = -
\begin{pmatrix}
\sigma & \sigma S \\
\sigma \Pi & \kappa
\end{pmatrix}
\begin{pmatrix}
\nabla V \\
\nabla T
\end{pmatrix}
$$

(7.1)
where $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, $S$ is the Seebeck coefficient and $\Pi = ST_0$ is the Peltier coefficient at a temperature $T_0$. The conservation of charge ($\vec{\nabla} \cdot \vec{J} = 0$) and Joule heating ($\vec{\nabla} \cdot \vec{Q} = J^2/\sigma$) are also incorporated. For the metallic elements, the input model parameters are the separately measured $\sigma$ and $S$, from which the electronic contribution to the thermal conductivity $\kappa_e$ and the Peltier coefficient $\Pi$ were determined using the Wiedemann-Franz (WF) and ORR relations, respectively [17]. In metallic systems the contribution of phonons to the thermal conductivity, at the temperatures of our experiments, can be ignored [1]. In graphene, this is not the case where the phonon contribution is much larger than the electronic contribution due to the strong C–C covalent bonds forming the graphene lattice [18]. In our model we use a thermal conductivity $\kappa_{gr} = 500 \text{ Wm}^{-1}\text{K}^{-1}$ that is independent of the charge carrier density [19]. The electrical conductivity $\sigma$ of the graphene is expressed using Drude’s semi-classical model as $\sigma = n|e|\mu$, where $n$ is the charge carrier density, $e$ is the electron charge and $\mu$ is the mobility of carriers. Various contributions to the charge carrier density $n$ of graphene were taken into account as [20]

$$n = \sqrt{n_{q}^2 + 4n_i^2},$$  

(7.2)

where $n_q = \alpha(V_g - V_0)$ is the electrostatically induced carrier density with $\alpha = 4.3 \times 10^{14} \text{ m}^{-2}\text{V}^{-1}$, $V_g$ is the gate voltage and $V_0$ is the gate voltage at the CNP, $n_i^2 = n_{pd}^2 + n_{th}^2$ is the residual carrier density due to charged inhomogeneities (puddles) $n_{pd}$ or charged impurities at the graphene/SiO$_2$ substrate [21, 22] and thermally excited carriers $n_{th} = \pi/(k_B T/\hbar v_F)^2$ at any $T > 0$ [23]. Using Mott’s relation $S = -eL_0T_0d\ln \sigma/dE$, where $L_0 = (\pi^2/3)(k_B/e)^2$ is the Lorenz number, we relate $S$ with $\sigma$ self-consistently [see Eq. (2.16) for detail]. The electrical and thermal interface resistances of both the Au/graphene ($K_{\text{Au-gr}} = 5 \times 10^7 \text{ Wm}^{-2}\text{K}^{-1}$) and graphene/SiO$_2$ ($K_{\text{gr-SiO}_2} = 2.5 \times 10^7 \text{ Wm}^{-2}\text{K}^{-1}$) interfaces [24, 25] are also taken into account. The mobility $\mu$ and residual charge carrier density $n_i$ are the only adjustable parameters in the model. While the first determines the width of the conductivity curve, the latter is related to the minimum conductivity $\sigma_{\text{min}} = n_i|e|\mu$ at the charge neutrality point.

### 7.4 Results and discussions

**Electrical conductivity measurement**

Figure 7.2(a) shows electrical conductivity $\sigma$ of single-layer graphene measured in a four-probe (4-probe) measurement configuration as a function of the gate voltage. Fitting the measured $\sigma$ with the Drude’s semiclassical expression $\sigma = ne\mu$, we
obtain a carrier mobility $\mu = 5000 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ and impurity carrier concentration $n_i = 2 \times 10^{11} \text{ cm}^{-2}$. These values of $\mu$ and minimum conductivity $\sigma_{\text{min}}$ of 0.27 mS are typical for good quality SiO$_2$ supported graphene layer [12, 20, 22]. Now, by relating this charge carrier density $n_i$ to the Fermi-energy $E_F$ of graphene as $E_F = \hbar v_F \sqrt{n\pi}/2$ (see Eq. (2.15) on page 26) we obtain a Fermi temperature $T_F = 429$ K corresponding to the Fermi energy broadening of 37 meV comparable to the thermal broadening at the temperature of our experiments. Such relatively small $T_F$ present difficulties, for instance, in the direct application of Mott’s relation which is an approximation for a degenerate electron gas [26]. By using similar analysis based on the 3D-FEM we obtain $n_i = 10^{11} \text{ cm}^{-2}$ and $\mu = 7000 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$, both values are close to those obtained earlier in the previous section. In the simulation of the Seebeck and Peltier effects, these predetermined values of $\mu$ and $n_i$ are used and the thermal conductivity of the graphene is kept as the only fitting parameter.

**Thermopower measurement**

In this measurement, we send a charge current $I$ through the heater [using contacts 1 and 2 in Fig. 7.2(d)] and measure the thermovoltage response $\Delta V$ across the graphene flake using the inner Au electrodes [contacts 3 and 6, with the contact closest to the heater (contact 3) at the ground potential]. Figure 7.2(b) shows the gate voltage dependence of the Seebeck coefficient $S_{\text{gr}} = -\frac{\Delta V}{\Delta T}$ of a single layer graphene for a charge current of 1 mA through the Joule-heater. Here the temperature bias $\Delta T = \Delta T_{TC1} - \Delta T_{TC2}$ across the flake is obtained by taking the difference between the temperature readings of the first thermocouple $\Delta T_{TC1}$ (contacts 4 and 7) and the second thermocouple $\Delta T_{TC2}$ (contacts 5 and 8). To that end we first characterize the response of these two thermocouples to the charge current through the heater as shown in Fig. 7.2(d). For a current of 1 mA through the heater, a temperature bias $\Delta T = 20$ mK across the central graphene region can be obtained.

The Seebeck coefficient $S_{\text{gr}}$ in Fig. 7.2(b) is largely positive (negative) in the hole (electron) regime and crosses through zero at the charge neutrality point (CNP). The vanishing $S_{\text{gr}}$ can be easily understood by noting that, at the CNP, the electron and hole carrier densities are equal and the thermovoltage contributions from each carrier types cancel. The maximum magnitude of $|S_{\text{gr}}| = 70 \mu \text{V/K}$ is comparable to earlier reported values [10, 12]. For comparison the Seebeck coefficient $S_{\text{Mott}}$ calculated from the measured electrical conductivity using Eq. (2.16) of chapter 2 is also shown in red. The estimate from Mott’s relation is often reported to be larger than the measured $S$ (a factor of two in our case) especially at higher temperatures [10, 12]. Mott’s relation is only valid at low temperatures $T/T_F \ll 1$ and the deviation specially around the CNP, where $T_F$ is small, is expected due to the failure of the Sommerfeld
approximation. At large gate voltages, the gate induced carrier density is very high thereby increasing $T_F$ by at least an order of magnitude. At such high carrier density regimes Mott’s relation agrees reasonably well with experimental measurements [12, 26].

Figure 7.2: (a) Electrical conductivity (symbols) with the calculated conductivity curve (red) using $\sigma = e n \mu$ (red line). (b) The measured Seebeck coefficient (symbols) along with the calculated $S$ (red line) using Mott’s formula $S = -eL_0 T_0 d \ln \sigma / dE$. The thermovoltage response in (b) is measured at twice the frequency of the excitation current ($2^{nd}$ harmonic signal). (c) The thermovoltage response of the NiCu-Au thermocouple due to Peltier heating/cooling as a function of the back gate voltage. The right axis shows the corresponding temperature calculated as $\Delta T_{TC} = V / (S_{NiCu} - S_{Au})$. (d) thermovoltage response of TC1 and TC2 to the current through the microfabricated Joule heater. At a current of 1mA, a temperature bias of 20 mK across the graphene flake is obtained. A charge current of r.m.s. 1 $\mu$A, 1 mA and 20 $\mu$A is used in (a), (b) and (c) respectively.
Peltier measurement

In the same device we also measured the Peltier cooling/heating at a graphene/Au interface due to the flow of a charge current \( I \). Depending on both the direction of

![Figure 7.3](image)

**Figure 7.3**: Calculated temperature profiles along the graphene flake in (a) the Seebeck measurement and (b) Peltier measurement configurations along with a surface temperature profile in the XY-plane (insets). The temperature profiles are taken along the white dashed-line in the surface temperature plot insets. For the Seebeck effect simulation a charge current of 1 mA is applied through the heater yielding a temperature bias \( \Delta T = 17 \text{ mK} \), as indicated by red arrows. In the Peltier effect measurement, a charge current of 20 \( \mu \text{A} \) is sent through the graphene using the Au electrodes thereby causing a maximum cooling (heating) of up to 50 mK at the two Au/gr interfaces. (c,d) Calculated gate voltage dependence of the thermopower and the Peltier coefficient and the comparison with the data (symbols) taken from Fig. 7.2. The calculated values, when scaled down by a factor of 2, fits well to the data.
current flow and/or the type of doping of the graphene, the Au/graphene interface is either cooled or heated resulting in a temperature change $\Delta T \propto \Pi_{\text{gr-Au}} I$, where $\Pi_{\text{gr-Au}} = \Pi_{\text{gr}} - \Pi_{\text{Au}}$ is the effective Peltier coefficient of the graphene ($\Pi_{\text{gr}}$) and Au ($\Pi_{\text{Au}}$) interface, where $\Pi_{\text{gr}} \gg \Pi_{\text{Au}}$. Figure 7.2(c) shows the gate voltage dependence of the temperature increase $\Delta T$ due to Peltier effect as measured by the NiCu-Au thermocouples for two different current directions. This temperature change shown here is obtained as $\Delta T_{TC} = V_{TC}/(S_{\text{NiCu}} - S_{\text{Au}})$, where $S_{\text{NiCu}}$ ($S_{\text{Au}}$) is the Seebeck coefficient of the NiCu (Au) and $V_{TC}$ is the measured thermovoltage response of the thermocouple. As expected the Peltier signal reverses sign when (i) the polarity of the current direction is reversed reflecting the linearity of the Peltier heat current and (ii) when $S_{\text{gr}}$ changes sign from the hole to electron regime.

Validation of the Thomson-Onsager reciprocity relation

To extract the Peltier coefficient $\Pi_{\text{gr}}$ and compare it with Seebeck coefficient $S_{\text{gr}}$, a good knowledge of the temperature profile at and around the Au/graphene interface is needed. Although a simple thermal resistor model that accounts for various heat losses through diffusion to either sides of the interface and through the SiO$_2$ to the Si substrate can be used, here we chose to use the 3D-FEM which gives a more accurate temperature profile.

Figure 7.3 show the results of the 3D-FEM where the line and surface temperature profiles for the Seebeck and Peltier measurements are shown, respectively. In the thermopower simulation [shown in Fig. 7.3(a)], for a charge current of 1 mA through the Joule heater, the calculated temperature bias across the graphene of 17 mK is in good agreement with the 20 mK experimentally obtained using the thermocouples. The gate voltage dependence of $S_{\text{gr}}$ calculated from the model is shown in Fig. 7.3(b) along with the experimentally measured thermopower taken from Fig. 7.2(b). A good agreement between the measured and calculated Seebeck coefficients is obtained when we scale down the results from the model by a factor of two. The maximum value of $S_{\text{gr}} = 80 \mu \text{V/K}$ is also close to the measured value with in 10%.

In the case of the Peltier effect, the temperature profile along the graphene flake [shown in Fig. 7.3(c)] shows a Peltier cooling (heating) of 60 mK at the graphene/Au interface for an electronic current flowing from the n-doped (p-doped) graphene to the Au. The magnitude of the calculated temperature change of 20 mK (symbols) is however a factor of two larger than measured [as shown in Fig. 7.3(d)]. This is expected because Mott’s relation tends to over estimate $S_{\text{gr}}$ by at least a factor of two [see Fig. 7.2(b)]. Hence the calculated Peltier response can be considered fairly accurate and we obtain a maximum Peltier coefficient of $\Pi_{\text{gr}} = 24 \text{ mV}$. The observation that both experiments could be modeled with identical sets of parameters
confirms the validity of the Thomson ORR relation with the main deviation arising from the failure of Mott’s relation. Another thermoelectric transport property that can lead to the deviation is $\kappa_{gr}$ that is reported to vary from 500 Wm$^{-1}$K$^{-1}$ [19] to 1000 Wm$^{-1}$K$^{-1}$ [27] for a substrate supported single layer graphene. However, we find that both the Seebeck and Peltier effect simulations are not sensitive to changes in $\kappa_{gr}$. For instance, an order of magnitude decrease from 5000 to 500 Wm$^{-1}$K$^{-1}$ brings about only a modest increase of 40% in the Peltier signal.

### 7.5 Conclusions

In summary, using a device architecture that allows for the direct measurement of small temperature changes, we presented room-temperature measurements of the Seebeck and Peltier effects in graphene field effect transistors. Building on earlier thermopower measurements of graphene, we also provided a purely electronic approach to the study of the Peltier cooling or heating mechanism in graphene. By comparing the separately measured Seebeck and Peltier coefficients we also validated the Thomson-Onsager reciprocity relation. Thermoelectric effects, when measured in a single device as we showed here, provide valuable information regarding the energy dependence of both electrical and thermal transport which otherwise is hidden in conventional transport measurements. Due to its unique properties graphene may provide richer understanding of underlying physics in spintronics, thermoelectrics and also spin caloritronics.
References

[16] The thermopower of the NiCu (constantan) was separately measured to be $-10 \mu V/K$, using similar technique as used for the graphene thermopower measurements.
7. Thermoelectric effects in graphene field effect transistors


