Thermopower of Graphene Nanoribbons in the Pseudodiffusive Regime

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Thermoelectric measurements for graphene ribbons are currently performed on samples that include atomic disorder via defects and irregular edges. In this work, we investigate the thermopower or Seebeck coefficient of graphene ribbons within the linear response theory and the Landauer formalism, and we consider the diffusive regime taken as a limit of the ribbon aspect ratio. We find that the thermopower and the electronic conductivity depend not only on the aspect ratio, but also on chemical potential and temperature, which are set here as key parameters. The obtained numerical results with temperature and doping are brought into contact with the thermoelectric measurements on disordered graphene ribbons with good agreement.

I. INTRODUCTION

Graphene has become a main subject of research due to its outstanding mechanical, thermal and electronic properties, among which the high electron mobility stands out. The increased carrier mobility and the long free path at room temperature establish graphene as a good building material to fabricate microwave transistors, photodetectors, and other electronic devices. Most of the proposed graphene devices consider ballistic electron propagation, so that the mean free path is longer than the size of the device, and electrons move across the sample without undergoing inelastic scatterings that break phase coherence. Although the ballistic transport regime has been studied both theoretically and experimentally, graphene has several types of defects, known to act as scattering centers within nanostructures that could modify their typical electronic properties.

Understanding the electron mobility of graphene samples requires studying the role of impurities and defects. Experiments on disordered two-dimensional graphene show a residual conductivity $4e^2/\pi h$ that arises from the electron density of states not vanishing at zero gate voltage. In agreement with the experiments, calculations using the semi-classical Boltzmann equation or the quantum Kubo formula for electron transmission show that dirty samples with a large concentration of charged impurities have a minimum conductivity value at low carrier density of about $4e^2/\pi h$ even for ideal pristine graphene. Furthermore, calculations using the Green-Kubo theory in long length ribbons having randomly distributed disorder, such as single and double vacancies, Stone-Wales defects and irregular ribbon-edge terminations, show that the phonon contribution to thermal conductance is negligible compared to the electron contribution.

Thermopower in the diffusive limit is measured in large and defective samples of exfoliated graphene and CVD graphene. The experimental thermopower measurements show a linear dependence with temperature, following the semi-classical Mott formula, which is also based on a weak electron-phonon interaction and a negligible phonon-drag effect. The questions that have to be answered next are: how the thermopower changes when the electron transport passes from the ballistic regime to the diffusive one, and how to characterize the diffusive limit in the thermopower calculations of long graphene samples. We herein study these questions using numerical and analytical approaches, and we find that when the conductivity enters the pseudodiffusive regime, the thermopower tends to be a constant directly proportional to temperature.

II. MODEL

The diffusive regime is reached for highly disordered samples when the average distance between scattering centers becomes larger than the typical coherence length $L_\phi$. Since the graphene experiments estimate the coherence length between 3 and 5 nm at 260 mK, atomistic models in the diffusive regime should involve a large number of atoms. Instead, without including the disorder explicitly, we consider the so-called “pseudodiffusive” regime defined when the transmission coefficients of the pristine system in a given configuration behaves as in a diffuse regime, even without the presence of disorder. This pseudo-diffusive regime can be achieved in several configurations, via electronic confinement through quantum dots and in graphene stripes being wide and short. We herein choose the latter option and study pristine metallic armchair nanoribbon of width $W$ in a tunnel junction configuration, with highly doped contacts and an undoped conductor section of length $L$. The leads are taken as the same nanoribbon doped using a large on-site potential, as shown in the model of Fig. [1]
and is geometrically parametrized using the width $W$ described by the Hamiltonian matrix $H$. The system is divided into three blocks. The central region describes the particle scattering between the R,L lead and the conductor.

The electronic conductance is thus defined as $G(E) = \frac{2e^2}{h} \mathcal{T}(E)$ and the conductivity $\sigma(E) = G(E) \times L/W$.

We then investigate the thermopower or Seebeck coefficient $S$. The thermopower is defined as the voltage drop induced by the temperature gradient at vanishing current, $S = -\Delta V/\Delta T|_{I=0}$, in the limit of $\Delta T \to 0$. The electric current is obtained within a single-particle picture using the Landauer approach

$$I = \frac{e}{\pi h} \int_{-\infty}^{\infty} T(E)(f_L(E) - f_R(E))dE,$$

where $T(E)$ is the transmission coefficient, and $f_{R,L}$ are the Fermi distributions of the right and left leads. The Seebeck coefficient is calculated in the linear response regime, i.e. $|\Delta T| \ll T$ and $|e\Delta V| \ll \mu$, with $\mu$ being the equilibrium chemical potential at the temperature $T$. It is given by

$$S(\mu, T) = \frac{1}{eT} \int_{-\infty}^{\infty} \left( -\frac{\partial f}{\partial E} \right) (E - \mu) T(E) dE.$$

B. Analytical Approach

Before discussing further the trends observed in different regimes, we elaborate on analytical expansions in series for the electronic transmission and the thermoelectric coefficient.

The total number $N$ of propagating modes depends on the ribbon width $W$, and the electronic transmission of a conducting channel $n$ can be formulated analytically. By applying the edge conditions of a metallic armchair ribbon to the Dirac equation, i.e. imposing that the wave functions values are zero in $y = 0$ and in $y = W$. The transmission probability per channel is given by

$$T_n = \frac{1}{\cosh^2(\pi nL/W)}, \quad n = 0, 1, 2...$$

and the electronic conductance $G$ can be written as

$$G = \left( \frac{2e^2}{h} \right) \sum_{n=0}^{N-1} T_n.$$

The Seebeck coefficient can be expressed using a Sommerfeld expansion for temperatures below the Fermi temperature. The Seebeck coefficient can be
III. DISCUSSION

To discuss the pseudodiffusive regimen, we have considered a tunnel junction configuration\cite{15}, in which the system between electrodes consists of a wide metallic nanoribbon parametrized by the length $L$ and the width $W (>> L)$. Our discussion focuses first on the $W/L \to \infty$ limit for the electronic conductivity $\sigma$ and the Seebeck coefficient $S$.

The conductivity $\sigma$ dependence on the aspect ratio $W/L$ is shown in Fig. 2(a). We find that the conductivity as a function of temperature undergoes small modifications. Our results for a fix temperature are consistent with the existing literature.\cite{10,11,12,13} When $W/L \to \infty$, the conductivity tends to a constant value, namely $\sigma_\infty = 4e^2/\pi h$. Note that using the same conditions, it was shown that the limit for the Fano factor is also a constant $F \to 1/3$\cite{10,11,12,13}. These findings are, therefore, the fingerprint of reaching a diffusive regime. We find that in practice, the pseudodiffusive limit is already reached when having $W/L > 4$, identified as the shaded region in Fig. 2 when the curves are saturated. Furthermore, in the pseudodiffusive regime obtained by increasing the $W/L$ ratio, the numerical calculations using the Landauer formula (Eq. 2) approach become closer to the analytical expansion of the conductivity given by Eq. 6. These results agree with the electronic transport experiments, which do not show temperature dependence in the conductivity of 2D graphene with temperatures below 300 K.\cite{13}

Figure 2(b) shows the different behavior of the Seebeck coefficient for graphene nanoribbons when the aspect ratio $W/L$ changes. In the ballistic limit, for small $W/L$, the values of Seebeck coefficient have a minimum. When the temperature increases, the $W/L$ ratio at which $S$ has a minimum decreases, while the $S_{\min}$ value increases.

The thermopower or Seebeck coefficient $S$, as defined in Eq. 4 through the transmission probability, depends directly on the temperature and indirectly on the aspect ratio $W/L$. In Fig. 2(b) we exposed these dependences. Similarly to conductivity, it is possible to identify the pseudodiffusive regime ($W/L > 4$) when the Seebeck coefficient becomes saturated. Our numerical results show that the Seebeck coefficient is saturated as the $W/L$ ratio increases, and the $S_\infty$ limit depends on the temperature, following Eq. 10. Because the used Sommerfeld expansion is valid for temperatures below the Fermi temperature, the analytical and numerical results differs slightly as the temperature increases. It is noteworthy that the experimental measurements estimated large values for the Fermi temperature as $T_F \sim 2490$ K in patterned epitaxial graphene\cite{15}, and $T_F \sim 1300$ K for free standing 2D graphene being doped $n < 10^{12}$cm$^{-2}$\cite{13}.

In the pseudodiffusive regimen, the Seebeck coefficient saturates because the curves converge asymptotically against the $W/L$ ratio. For large $W/L$ ratios, the Seebeck coefficient is highly dependent on the temperature, a result in agreement with the semi-classical Mott
formula but not expected for a ballistic system. In addition to the well-known limits \( \sigma \to 4e^2/\pi \hbar \) and \( F \to 1/3 \), our results reveal other trend for electronic transport in the diffusive regime, that is, \( S \to \frac{(\pi k_B)^2}{4e} T \) as defined in Eq. [10] which shows the a linear dependence on temperature of the Seebeck coefficient.

Finally, we comment on the transition between ballistic and pseudodiffusive regimes looking at numerical calculations of conductivity and Seebeck coefficient versus chemical potential. Figure 3 displays the behavior of \( \sigma \) and \( S \) depending on the chemical potential \( \mu \) for different aspect ratios \( W/L \), using a ribbon with \( N = 35 \) and a fix temperature of \( T = 200 \) K. In general, the conductivity decreases as the aspect ratio increases. In the pseudodiffusive region, for example with \( W/L \sim 10 \), the conductivity is linear with the chemical potential. This trend is already indicated in a smaller range of \( W/L \) ratios looking at a narrow energy window, as shown in the inset for the case of \( W/L \sim 3 \). The Seebeck coefficient \( S \) in the ballistic regimen around the Fermi level is characterized by a maximum followed by a minimum. However, when the aspect ratio increases in the pseudodiffusive regime, the local maximum values decrease and expand reaching an almost constant value over the entire energy range around the Fermi energy.

### IV. FINAL REMARKS

In summary we reproduce the well-known limits \( \sigma \to 4e^2/\pi \hbar \) and \( F \to 1/3 \) in the diffusive regime. Our results on Seebeck coefficient (or thermopower) allow us to add new features to the electronic transport of graphene nanoribbons in the diffusive regime. We find that \( S \to \frac{(\pi k_B)^2}{4e} T \) as defined in Eq. [10] so that the Seebeck coefficient depends linearly on the temperature. In addition, we have performed numerical calculations, which in the asymptotic pseudodiffusive limit are in good agreement with the analytical expressions. Notice also that although we are dealing with wide and short metallic tunnel junctions, our results are following the estimates using the Boltzman equation for large and disordered systems, a fact which fulfills the semi-classical Mott formula.

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