Charge and Phonon Transport in Suspended Monolayer Graphene

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Abstract Thermal effects are playing a crucial role for the design of electron nanoscale devices. The present contribution deals with charge and phonon transport under an applied external electric field in a suspended monolayer of graphene. A major question is represented by the phonon-phonon collision operator involving in general a three particle scattering mechanism. To model the phonon-phonon interactions a relaxation time approximation is employed. This requires the introduction of a local equilibrium phonon temperature whose definition is still a matter of debate for a general non equilibrium situation. Here, two different approaches are presented and discussed.

1 Introduction

Graphene is one of the most promising materials for future nano-electronics because of its unique electrical and thermal properties. It has been increasingly investigated from different points of view. A correct mathematical description of transport phenomena in graphene is fundamental and there have been a lot of attempts and approaches, starting from the well-established results for other traditional semiconductor materials and devices. In particular, kinetic and macroscopic models have been applied, see for example [1–5]. Also stochastic approaches, as the Direct

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Simulation Monte Carlo (DSMC), are consolidated methods for numerically solving transport equations in graphene. However, many of them do not properly take into account the Pauli exclusion principle [6], that in graphene is no longer negligible for the high values of the electron densities. This problem has been overtaken by a new DSMC procedure which correctly includes the Pauli principle. Cross-validations with deterministic solutions, e.g. the Discontinuous Galerkin-based ones, confirm that this approach is completely satisfactory [7]. The new DSMC approach allows us to describe electron transport in graphene also in cases when graphene is on several types of substrates [8, 9].

Together with the correct inclusion of the Pauli exclusion principle into the charge transport simulations, to have a satisfactory and complete description of transport phenomena in graphene, it is necessary an adequate treatment of the phonon-phonon collision operators. Its complete form involves at least a three particle kernel and this makes the numerics rather complicated. A way to overcome the problem is to replace the original collision operators with a simpler relaxation time approximation. This requires the introduction of a local phonon temperature whose definition is still a matter of debate for a general non equilibrium situation. In this paper two different approaches for defining the local equilbrium phonon temperature are introduced and discussed on the basis of the results reported in [5] and [10, 11].

2 Kinetic Model

Graphene is made of carbon atoms arranged in a honeycomb hexagonal lattice. The most part of electrons are located in the wave vector space around the *Dirac points* K and K', which are the vertices of the hexagonal primitive cell of the reciprocal lattice. At the Dirac points, the valence and conduction band touch each other and, therefore, graphene is a semimetal. In the proximity of the Dirac points the energy bands for electrons can be approximated by a conical band structure and the electrons behave as massless Dirac fermions [12]. We consider Fermi levels high enough to neglect the dynamics of the electrons in the valence band, that we consider fully occupied. This situation is similar to an n-type doping for the traditional semiconductors. Around the equivalent Dirac points the band energy ε_ℓ is approximated by a linear relation

$$\varepsilon_\ell = \hbar \, v_F \, |\mathbf{k} - \mathbf{k}_\ell| \,, \tag{1}$$

and the group velocity is given by

$$\mathbf{v}_\ell = \frac{1}{\hbar} \, \nabla_{\mathbf{k}} \, \varepsilon_\ell \,.$$

Here $\mathbf{k}$ is the electron wave-vector, v_F is the (constant) Fermi velocity, $\hbar$ the Planck constant divided by $2\,\pi$, and $\mathbf{k}_\ell$ is the position of the Dirac point $\ell = K, K'$.

In a semiclassical kinetic setting questa virgola la toglierei, for the electrons in the conduction band, the charge transport in graphene is described by two Boltzmann equations, for the K and K' valleys.

$$\frac{\partial f_\ell(t, \mathbf{x}, \mathbf{k})}{\partial t} + \mathbf{v}_\ell \cdot \nabla_{\mathbf{x}} f_\ell(t, \mathbf{x}, \mathbf{k}) \ -\frac{e}{\hbar} \mathbf{E} \cdot \nabla_{\mathbf{k}} f_\ell(t, \mathbf{x}, \mathbf{k}) = \left.\frac{df_\ell}{dt}(t, \mathbf{x}, \mathbf{k})\right|_{e-ph} \quad (2)$$

where $f_\ell(t, \mathbf{x}, \mathbf{k})$ represents the distribution function of charge carriers in the valley ℓ (K or K'), at position $\mathbf{x}$, time t, and with wave-vector $\mathbf{k}$. We denote by $\nabla_{\mathbf{x}}$ and $\nabla_{\mathbf{k}}$ the gradients with respect to the position and the wave-vector, respectively. e is the elementary (positive) charge and $\mathbf{E}$ is the externally applied electric field.

All the scattering events between electrons and phonons are described by the collision term, at the right hand side of (2). The scattering of electrons can be with longitudinal or transversal, acoustic and optical phonons, *LA*, *TA*, *LO* and *TO*, respectively. Both the acoustic and optical phonon scatterings are intra-valley and intra-band. Eventually, one has to take into account also the scattering of electrons with *K* phonons which is inter-valley and, therefore, pushes electrons from a valley to the nearby one. The general form of the collision term can be written as

$$\left.\frac{df_\ell}{dt}(t, \mathbf{x}, \mathbf{k})\right|_{e-ph} = \sum_{\ell'}\left[\int_\mathcal{B} S_{\ell', \ell}(\mathbf{k}', \mathbf{k})\, f_{\ell'}(t, \mathbf{x}, \mathbf{k}')\, (1 - f_\ell(t, \mathbf{x}, \mathbf{k}))\, d\mathbf{k}'\right.$$

$$\left. -\int_\mathcal{B} S_{\ell, \ell'}(\mathbf{k}, \mathbf{k}')\, f_\ell(t, \mathbf{x}, \mathbf{k})\, \left(1 - f_{\ell'}(t, \mathbf{x}, \mathbf{k}')\right) d\mathbf{k}'\right],$$

where the total transition rate $S_{\ell', \ell}(\mathbf{k}', \mathbf{k})$ is given by the sum of the contributions of the several types of scatterings [5]:

$$S_{\ell', \ell}(\mathbf{k}', \mathbf{k}) = \sum_\mu \left|G_{\ell', \ell}^{(\mu)}(\mathbf{k}', \mathbf{k})\right|^2 \left[\left(g_\mu^- + 1\right) \delta\left(\varepsilon_\ell(\mathbf{k}) - \varepsilon_{\ell'}(\mathbf{k}') + \hbar\,\omega_\mu\right)\right.$$

$$\left. +g_\mu^+ \,\delta\left(\varepsilon_\ell(\mathbf{k}) - \varepsilon_{\ell'}(\mathbf{k}') - \hbar\,\omega_\mu\right)\right]. \quad (3)$$

The index μ labels the μth phonon species. The $\left|G_{\ell', \ell}^{(\mu)}(\mathbf{k}', \mathbf{k})\right|^2$'s are the electron-phonon coupling matrix elements, which describe the interaction mechanism by which an electron goes, from the state of wave-vector $\mathbf{k}'$ belonging to the valley ℓ' to the state of wave-vector $\mathbf{k}$ belonging to the valley ℓ, through the emission or absorption of a μth phonon. The symbol δ denotes the Dirac distribution, ω_μ is the μth phonon frequency, $g_\mu(\mathbf{q})$ is the phonon distribution for the μ-type phonons with $\mathbf{q}$ the phonon wave-vector belonging to the Brillouin zone $\mathcal{B}$. In (3), $g_\mu^\pm = g_\mu\left(\mathbf{q}^\pm\right)$, where $\mathbf{q}^\pm = \pm\left(\mathbf{k}' - \mathbf{k}\right)$, stemming from the momentum conservation. The K and K' valleys can be treated as equivalent and in the following we consider the population of one single valley.

Similarly, the dynamics of the phonon populations is described by solving the following Boltzmann equations for the phonon distributions $g_\mu(t, \mathbf{x}, \mathbf{q})$

$$\frac{\partial g_{op}}{\partial t} = C_{op}, \quad op = LO, TO, K, \tag{4}$$

$$\frac{\partial g_{ac}}{\partial t} + \mathbf{c}_{ac} \cdot \nabla_{\mathbf{x}} g_{ac} = C_{ac}, \quad ac = LA, TA, \tag{5}$$

$\mathbf{c}_{ac} = \nabla_{\mathbf{q}} \omega_{ac}$ is the acoustic phonon group velocity, $\hbar \omega_{ac}$ being the phonon energy and $\mathbf{q}$ the phonon wave vector.

The group velocity of the optical phonons disappears because of the Einstein approximation $\hbar \omega_{op} \approx$ const, which can be used for them, while, regarding the acoustic phonons, the Debye approximation can be used: $\omega_{ac} = c_{ac} |\mathbf{q}|$, with c_{ac} the sound speed of the sth acoustic branch.

In principle also the Z phonons should be included although they do not interact with electrons but they contribute to the total crystal temperature. In the present article the Z phonons will be neglected for the sake of simplicity.

The phonon collision term splits in two parts

$$C_\mu = C_\mu^{p-e} + C_\mu^{p-p}, \quad \mu = LA, TA, LO, TO, K. \tag{6}$$

C_μ^{p-e} represents the phonon-electron collision operator, while C_μ^{p-p} describes the phonon-phonon interactions, that are a very difficult problem to deal with from a numerical point of view. For this reason they are usually treated by means of a Bhatnagar-Gross-Krook (BGK) approximation [13]

$$C_\mu^{p-p} = -\frac{g_\mu - g_\mu^{LE}}{\tau_\mu}.$$

This describes the relaxation of each phonon branch towards an equilibrium condition, that is represented by a local equilibrium distribution g_μ^{LE}, whose temperature, we refer to as the local temperature T_L, is the same for each phonon population.

We assume that the local equilibrium phonon distributions are given by Bose-Einstein distributions

$$g_\mu^{LE} = \left[e^{\hbar \omega_\mu / k_B T_L} - 1 \right]^{-1}. \tag{7}$$

The functions $\tau_\mu = \tau_\mu(T_\mu)$ are the temperature dependent phonon relaxation times. We remark that each relaxation time is supposed to depend only on the temperature T_μ of the same branch.

If we know the phonon distributions g_μ's, we can calculate the average phonon energy densities

$$W_\mu = \frac{1}{(2\pi)^2} \int_{\mathcal{B}} \hbar \omega_\mu \, g_\mu \, d\mathbf{q}, \tag{8}$$

and the temperatures T_μ of each phonon branch are determined from

$$\int_{\mathcal{B}} \hbar\omega_\mu g_\mu(\mathbf{q}) d\mathbf{q} = \int_{\mathcal{B}} \hbar\omega_\mu \left[e^{\hbar\omega_\mu / k_B T_\mu} - 1 \right]^{-1} d\mathbf{q}. \tag{9}$$

From the general properties of the phonon collision operators, the relation

$$\sum_\mu \frac{W_\mu - W_\mu^{LE}}{\tau_\mu} = 0 \tag{10}$$

holds, where W_μ^{LE} is calculated by means of (7). *T_L is obtained by numerically solving the non linear relation arising from (10).*

It is possible to prove that (10) admits a unique solution. For further details we refer to [11] where the previous approach has been adopted to devise a simulation scheme for the electron-phonon transport in graphene.

3 Alternative Form of the Local Temperature

The concept of non equilibrium temperature is a subtle topic and still a matter of debate [14, 15]. In the previous section we have introduced the local temperature by the relation (10) which stems from the properties of the phonon-phonon collision operator. The rational is that the collision operator *pushes* the system, in a characteristic time related to the relaxation times, toward an equilibrium state with a single global temperature. However, in statistical mechanics one of the most reasonable and adopted way to generalise the concept of temperature in a non equilibrium state is relating T_L to the Lagrange multipliers associated to the energy constraint.

For phonon transport in graphene the approach based on the Lagrange multipliers has been followed in [5] (to which the interested reader is referred to for the details) within the application of the Maximum Entropy Principle (MEP) (see [16] for a review of MEP in semiconductors). Let us recall here the main steps.

The temperature of each phonon branch is introduced as in the previous section while the local temperature is defined as follows [13, 17]. *The temperature T_L^* is the common temperature we must assign to each species in order to have*

$$\sum_\mu W_\mu = \sum_\mu W_\mu^{LE}. \tag{11}$$

In other words, T_L^* is the common temperature each phonon species should have if they would be in local thermodynamic equilibrium among them in order to preserve the total energy.
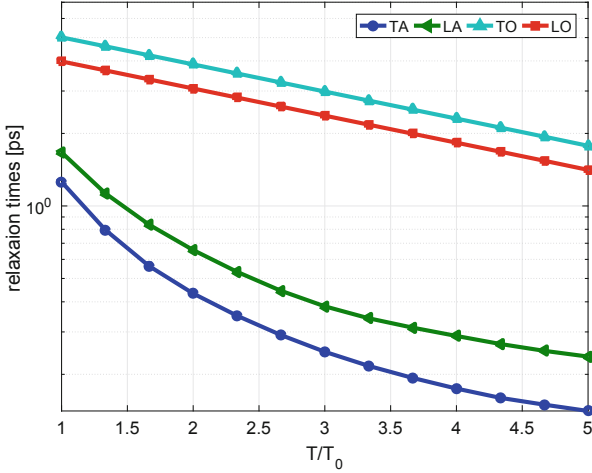
Fig. 1 Relaxation times versus the local temperature normalized with respect to the room one T_0

The new and the old definitions of local temperature are equivalent if all the relaxation times are equal, that is

$$\tau_\mu = \tau, \quad \mu = LO, TO, LA, TA, K, \tag{12}$$

but this assumption is not compatible with experimental data, as clearly indicated by Fig. 1. As a consequence, the two definitions of temperature do not coincide.

T_L^* is related only to the energy of the system and does not take into account any scattering mechanism. If T_L^* is assumed as the correct definition of local temperature, then the relation (10) must be considered as a constraint on the relaxation times.

In the model formulated in [5] for charge and phonon transport in graphene, a certain number of moments of electron and phonon distributions are used as fundamental variables, and the extra fluxes and the production terms, which appear in the corresponding balance equations, are additional unknown quantities and require constitutive relations in terms of the fundamental variables. By resorting to MEP, the electron and phonon occupation numbers can be estimated by the maximum entropy distributions f_{MEP} and $g_{\mu,MEP}$, $\mu=LO, TO, K, LA, TA$, which solve the following maximization problem:

$$\max_{f, g_\mu} S[f, g_\mu],$$

under the constraint that a certain number of moments, the fundamental variables, are known.

$S[f, g_\mu]$ is the total entropy which depends on the electron and phonon distribution functions f, g_μ and whose expression is reported in [5].

If in particular for the phonons we choose the following moments

$$W_{op} = \frac{1}{(2\pi)^2} \int_{\mathcal{B}} \hbar \omega_{op} g_{op} \, d\mathbf{q},$$

$$\mathbf{P}_{op} = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \hbar \mathbf{q} g_{op} \, d\mathbf{q}, \; op = LO, TO, K, \tag{13}$$

$$W_{ac} = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \hbar \omega_{ac} g_{ac} \, d\mathbf{q},$$

$$\mathbf{Q}_{ac} = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \hbar \omega_{ac} \mathbf{c}_{ac} g_{ac} \, d\mathbf{q}, \; ac = LA, TA, \tag{14}$$

and, solving the above constrained maximization problem, we get

$$g_{op,MEP} = \frac{1}{\exp\left(\lambda_{W_{op}} \varepsilon_{op} + \hbar \, \mathbf{q} \cdot \lambda_{\mathbf{P}_{op}}\right) - 1}, \quad op = LO, TO, K,$$

$$g_{ac,MEP} = \frac{1}{\exp\left(\lambda_{W_{ac}} \varepsilon_{ac} + \varepsilon_{ac} \, \mathbf{c}_{ac} \cdot \lambda_{\mathbf{Q}_{ac}}\right) - 1}, \quad ac = LA, TA,$$

where the λ's are the Lagrange multipliers arising from the presence of the constraints.

In order to manage the problem of inverting the constraints, we linearize the occupation numbers around their isotropic part, obtaining

$$g_{op,MEP} \approx \frac{1}{e^{\lambda_{W_{op}} \varepsilon_{op}} - 1} \left[1 - \frac{e^{\lambda_{W_{op}} \varepsilon_{op}}}{e^{\lambda_{W_{op}} \varepsilon_{op}} - 1} \hbar \mathbf{q} \cdot \lambda_{\mathbf{P}_{op}} \right], \; op = LO, TO, K, \tag{15}$$

$$g_{ac,MEP} \approx \frac{1}{e^{\lambda_{W_{ac}} \varepsilon_{ac}} - 1} \left[1 - \frac{e^{\lambda_{W_{ac}} \varepsilon_{ac}}}{e^{\lambda_{W_{ac}} \varepsilon_{ac}} - 1} \varepsilon_{ac} \mathbf{c}_{ac} \cdot \lambda_{\mathbf{Q}_{ac}} \right], \quad ac = LA, TA. \tag{16}$$

By substituting (15)–(16) into the constraints (13)–(14) and by solving them with respect to the Lagrange multipliers, one finds

$$\lambda_{W_{op}} = \frac{1}{\varepsilon_{op}} \ln\left(1 + \frac{y \varepsilon_{op}}{W_\eta}\right), \; \eta = LO, TO, K, \tag{17}$$

$$\lambda_{W_{ac}} = \left(\frac{4\pi y \zeta(3)}{\hbar^2 c_{ac}^2}\right)^{\frac{1}{3}} W_{ac}^{-\frac{1}{3}}, \quad ac = LA, TA \tag{18}$$

$$\lambda_{\mathbf{P}_{op}} = -\frac{A^2 \varepsilon_{op}^2}{4\hbar^2 A_1} \frac{y}{W_{op}(W_{op} + Ay \varepsilon_{op})} \mathbf{P}_{op}, \quad op = LO, TO, K, \tag{19}$$

$$\lambda_{\mathbf{Q}_{ac}} = -\frac{2}{3} \left(\frac{4\pi y \zeta(3)}{\hbar^2 c_{ac}^8} W_{ac}^{-4}\right)^{\frac{1}{3}} \mathbf{Q}_{ac}, \quad ac = LA, TA, \tag{20}$$

where $y = \frac{1}{(2\pi)^2}$, $\zeta(\cdot)$ is the zeta function, $A = \frac{8\sqrt{3}}{9}\frac{\pi^2}{a_0^2}$, $A_1 = \frac{20\sqrt{3}}{729}\frac{\pi^4}{a_0^4}$, with $a_0 = 0.142$ nm the nearest neighbor distance between the atoms in graphene.

At equilibrium the phonon temperatures are related to the corresponding Lagrange multipliers by means of

$$T_\mu = \frac{1}{k_B \lambda_{W_\mu}}, \quad \mu = LO, TO, K, LA, TA.$$

If we assume that such relations hold even out of equilibrium, the definition of T_L^* can be given in terms of the Lagrangian multipliers as follows.

Definition 3.1 The local temperature of a system of two or more branches of phonons is $T_L^* := \frac{1}{k_B \lambda_{W_L}}$, where λ_{W_L} is the common Lagrange multiplier the occupation numbers of the branches, taken into account, would have if they were in the local thermodynamic equilibrium corresponding to their total energy density, that is

$$W(\lambda_{W_L}) := \sum_\mu W_\mu(\lambda_{W_L}) = \sum_\mu W_\mu(\lambda_{W_\mu}),$$

where the sum is extended to the considered branches and the functions $W_\mu(\lambda_{W_\mu})$ are found from expressions (17)–(18).

In other words, we require that T_L^* is such that by evaluating all the average phonon energy densities with the Lagrange multiplier given by $1/k_B T_L^*$ and by summing up, one gets the value of the total average energy density.

A comparison with experiments is not easy because it is not clear what exactly is measured by the instruments. The comparison between T_L and T_L^* is still under investigation by the authors. The numerical results will be the argument of a forthcoming article.

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