Electronic transport in graphene: A semi-classical approach including midgap states

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Using the semi-classical Boltzmann theory, we calculate the conductivity as function of the carrier density. As usually, we include the scattering from charged impurities, but conclude that the estimated impurity density is too low in order to explain the experimentally observed mobilities. We thus propose an additional scattering mechanism involving midgap states which leads to a similar k-dependence of the relaxation time as charged impurities. The new scattering mechanism can account for the experimental findings such as the sublinear behavior of the conductivity versus gate voltage and the increase of the minimal conductivity for clean samples. We also discuss temperature dependent scattering due to acoustic phonons.

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I. INTRODUCTION

Electronic transport through two-dimensional graphene sheets has attracted incessant attention ever since the first experimental measurements on a Hall geometry were performed by Geim and coworkers about three years ago. This is due to some spectacular findings like the universal minimal conductivity at the Dirac point and the high mobility of the samples which is basically independent of doping and temperature. Different experimental setups, i.e., electrical field versus chemical doping, also give rise to different theoretical models. For recent qualitative reviews on both the experimental and theoretical status of the field, see Ref. \textsuperscript{5,6,7}

So far, the scattering mechanism which determines the transport properties has not unambiguously been identified, but there is strong evidence that long-range Coulomb scatterers can account for many of the experimental findings. \textsuperscript{8,9,10,11} It was shown within the Boltzmann formalism that the conductivity scales linear with the carrier density if one assumes charged impurities in the SiO$_2$-substrate close to the graphene-sheet.\textsuperscript{8} This semi-classical approach was also applied to systems close to the Dirac point and in the presence of adsorbed molecules.\textsuperscript{12}

Recently, it was claimed that a Boltzmann theory with long-range Coulomb scatterers can account for all experimental findings if one renormalizes the carrier density close to the Dirac point due to potential fluctuations.\textsuperscript{13,14} The theory predicts a non-universal behavior of the minimal conductivity at the Dirac point which nevertheless coincides with the experimentally observed value of $4e^2/h$ for “dirty” samples. This is in contrast to numerical studies based on the Kubo-formalism by Nomura and MacDonald\textsuperscript{15} who show that the conductivity is a function of $n_F/n_i$ with $n_F$ the impurity density, thus finding universal behavior when the carrier density $n$ goes to zero. The main criticism of Ref.\textsuperscript{13} is the high density of charged impurities $n_i > 10^{12}$ cm$^{-2}$ needed to match the experimentally observed mobilities, not likely to be present in an insulator such as SiO$_2$.\textsuperscript{16}

In this article, we propose a new scattering mechanism originating from midgap states which may be formed due to vacancies, cracks, boundaries or impurities in the substrate with a high potential difference with respect to the graphene sheet.\textsuperscript{17,18} They also occur in corrugated graphene.\textsuperscript{19} The phase shift resulting from these types of disorder must approach zero for wave vectors close to the Dirac point. In contrast to the phase shift due to a short-range contact potential, this behavior is not linear but logarithmic.\textsuperscript{20,21} The resulting scattering time is, therefore, proportional to $k$ up to logarithmic corrections. It is interesting to note that this behavior is also found for a two-dimensional (“non-relativistic”) electron gas\textsuperscript{22} and in corrugated graphene\textsuperscript{23} where the focus was laid on the resulting random gauge field.

Within the Boltzmann approach, the new mechanism can account for: a) quasi-universal minimal conductivity for dirty samples; b) a higher minimal conductivity for cleaner samples; c) sub-linear behavior of the conductivity as function of the gate voltage. We further obtain realistic values for the mobility assuming an equal concentration for Coulomb scatterers and vacancies of order $n_i \sim 10^{10} - 10^{11}$ cm$^{-2}$.

The paper is organized as follows. In Sec. II we will first introduce the Boltzmann approach and comment on its applicability to graphene, i.e., to chiral Dirac Fermions. In Sec. III we discuss the density of states in the presence of midgap states, needed to estimate the transport properties close to the Dirac point. In section IV we calculate the relaxation time and electrical conductivity for the various scattering mechanism including acoustical phonons. In section V we discuss the ac-conductivity, the thermal conductivity and the thermopower for the new scattering mechanism including midgap states and present numerical results in section VI. We close with conclusions and remarks.
II. BOLTZMANN EQUATION

A. Collision-free Boltzmann equation

We start by showing that the Boltzmann equation description leads to the same plasmon spectrum as the more used many-body methods. This shows that a semi-classical approach for the transport properties of graphene is accurate.

The Boltzmann equation is described in terms of the electronic distribution function $f_k$. Within this semi-classical approach, $f_k$ depends on space $r$ and time $t$, i.e.,

$$f_k = f_{k(t)}(r,t) .$$ (1)

Looking at time scales shorter than the lifetime of the quasi-particles, the number of quasi-particles in the state $k$ is conserved. Via the continuity equation $\dot{f}_k + \nabla_r \cdot j_k = 0$ with $j_k = v_k f_k$ denoting the particle current, one arrives at the collision-free Boltzmann equation. With $k = e\nabla_r \varphi$ where $\varphi$ is the scalar potential of the internal electric field, this reads in Fourier space as

$$(-i\omega + iq \cdot v_k)f_k(q,\omega) = icq \cdot v_k(-\partial f_k/\partial \epsilon_k)\varphi(q,\omega) .$$ (2)

To investigate screening properties, an external potential $\varphi^{ext}(q,\omega)$ is assumed. To linear order in the total potential $\varphi$, the induced density is then given by

$$\rho^{ind}(q,\omega) = \frac{4}{A} \sum_k \frac{q \cdot v_k}{\omega - q \cdot v_k}(-\partial f_k/\partial \epsilon_k)(-e\varphi(q,\omega)) ,$$ (3)

where $A$ is the area of the graphene sheet and spin and valley degeneracies have been included.

The induced potential is obtained by $(-e)\varphi^{ind}(q,\omega) = V_q \rho^{ind}(q,\omega)$ with $V_q = \frac{1}{2\pi q^2}$ the two-dimensional Fourier transform of the Coulomb potential. For the dielectric function $\epsilon(q,\omega) = \varphi^{ext}(q,\omega)/\varphi(q,\omega)$, one then obtains in the long-wavelength limit $v_F q \ll \omega$ the following expression:

$$\epsilon(q,\omega) \approx 1 - \frac{V_q}{\omega^2} \sum_k (q \cdot v_k)^2(-\partial f_k/\partial \epsilon_k)$$

$$= 1 - \frac{V_q q^2 v_F^2}{\omega^2} \frac{1}{\pi}$$ (4)

Plasmon excitations are given by $\epsilon(q,\omega) = 0$ which leads to the plasmon dispersion

$$\omega = \sqrt{\frac{e^2}{2m_0}v_F q} .$$ (5)

This relation including the prefactor is also obtained from a standard tight-binding model of graphene where the dielectric function is calculated within the random-phase approximation. Our subsequent results should thus be valid even close to the neutrality point as long as $k_F \ell \gg 1$ ($\ell$ the mean free path), i.e., the chirality of the Dirac fermions only enters in the expression for the transition rate (see Eq. 21). For a quantitative analysis starting from a two-band model, see Ref. 25.

B. Collision term

We now include the possibility of changing the quantum state $k$ by introducing a collision term which is usually facilitated by the relaxation-time approximation.

$$-\frac{\partial f_k}{\partial t} \bigg|_{scatt.} = \frac{g_k}{\tau_k} ,$$ (6)

where $f_k - f^0_k = g_k$.

Applying an electric field $E$ to the sample, the solution of the linearized Boltzmann equation then reads

$$g_k = -\frac{\partial f^0_k(\epsilon_k)}{\partial \epsilon_k} e\tau_k v_k \cdot E ,$$ (7)

and the electric current reads

$$J = \frac{4}{A} \sum_k e v_k g_k .$$ (8)

Since at low temperature the following relation $-f^0(\epsilon_k)/\partial \epsilon_k \approx \delta(\nu_F h(k - k_F))$ holds, we obtain for the conductivity with the Fermi velocity $v_F$ the well-known formula

$$\sigma = \frac{e^2 v_F^2}{2} \rho(E) \tau_{k_F} .$$ (9)

In the following, we will give expressions for the density of states $\rho(E)$ and the relaxation time $\tau_{k_F}$. We then discuss the electrical conductivity in the low- and high-density limit.

III. DENSITY OF STATES

The density of states per unit area of clean graphene is given by

$$\rho_0(E) = \frac{2|m|}{(h v_F)^2} ,$$ (10)

where spin and valley degeneracies have been included.

Due to potential disorder this linear behavior becomes sub-linear, though the density of states at the Dirac-point is still zero. More important are local defects in form of vacancies which were first discussed in Ref. 30. Within a self-consistent Born approximation (CPA), it was shown that the relaxation time depends linearly on the mean free path, i.e., $\tau \sim \ell/v_F$. For the mean free path we have $\ell \sim 1/\sqrt{n_i}$, where $n_i$ stands for the impurity density due to vacancies, cracks, etc. In order to obtain
an universal minimal conductivity, the density of states close to the Dirac point must be given by \( \rho \sim 1/(\hbar v_F) \).

This behavior is also obtained from a phenomenological approximation. For this, it is important to note that vacancies gives rise to localized states which decay algebraically. These states hybridize due to the overlap with localized states of other vacancies. The energy scale is given by the mean distance between vacancies and approximated by the gain of energy due to the new boundary conditions.

This energy scale is approximated as follows. The linearized tight-binding Hamiltonian for a graphene sheet with circular symmetry is given by

\[
H_s = \begin{pmatrix}
0 & e^{i\phi}(-is\partial_r + \frac{1}{r}\partial_\phi) \\
e^{-is\phi}(-is\partial_r + \frac{1}{r}\partial_\phi) & 0
\end{pmatrix},
\]

where \( s = \pm 1 \) denotes the two valleys. At non-zero energy, the general solution is given by the Bessel and Hankel functions. Considering only one valley \( s = 1 \), the general wave-function in graphene at low energies is thus given by

\[
\psi_k(R, \phi) = A \begin{pmatrix} J_0(kR) \\ -iJ_1(kR)e^{i\phi} \end{pmatrix} + B \begin{pmatrix} Y_0(kR) \\ -iY_1(kR)e^{i\phi} \end{pmatrix}.
\]

A simple model for vacancies of radius \( R_0 \) and localized on the radius \( R_3 \) now assumes that the first component becomes zero at the inner boundary \( R_0 \) and the second component at the outer boundary \( R_1 \), thus assuming zig-zag edges on different sublattices. This leads to the following quantization condition for \( k \):

\[
J_0(kR_0)Y_1(kR_1) - Y_0(kR_0)J_1(kR_1) = 0.
\]

For \( kR_1 \ll 1 \), the lowest momentum is then given by

\[
k \sim \frac{1}{R_1} \left( \frac{1}{\sqrt{|\ln(R_0/R_1)|}} \right),
\]

which defines the width of the localized band

\[
E_{\text{loc}} = \frac{\hbar v_F}{R_1 \sqrt{|\ln(R_0/R_1)|}}.
\]

The density of states at zero energy is thus approximated by

\[
\rho(0) = \frac{\sqrt{|\ln(R_0/R_1)|}}{\hbar v_F R_1}.
\]

Since \( R_1 \) is related to the average distance between the vacancies, we have \( \rho(0) \sim (n_i |\ln n_i|)^{1/2} \). Notice that the CPA calculation of Ref. 30 does not capture the logarithmic correction. We will therefore approximate the density of states as

\[
\rho(E) = \alpha \frac{\sqrt{n_i}}{\hbar v_F} g_c(E_{\text{loc}} - |E|) + \frac{2|E|}{\pi(\hbar v_F)^2}
\]

where the density of states at zero energy is approximated by

\[
\rho(0) \sim \frac{2\pi}{\hbar} v_F k_F \tau_{k_F}.
\]

Close to the Dirac point \( E_F < E_{\text{loc}} \), we obtain the minimal conductivity

\[
\sigma_{\text{min}} = \frac{2\pi e^2}{h} \frac{v_F}{10} \alpha \tau_{k_F}.
\]

Notice that we obtain the same formula as for high electronic densities by introducing a minimal Fermi wave-vector \( k_{\text{min}} \sim \sqrt{n_i} \). The minimal Fermi wave-vector with \( k_F \ell \gg 1 \) can be related to self-doping effects induced by the very same mechanism which is invoking midgap states.\( ^{30} \) and we will show in the following that a crossover from a linear to constant behavior of the conductivity versus gate voltage takes place.

If one believes that close to the neutrality point the system also behaves in a diffusive way, i.e., that the experimentally observed negatively and positively charged puddles form a macroscopic network,\( ^{30} \) then even for low impurity densities \( n_i \sim 10^{10}\text{cm}^{-2} \) with \( k_F \ell \approx 1 \) one can use our estimates (up to a constant of order 1). Still, we cannot rule out the existence of another regime where the Boltzmann approach is invalid and e.g. percolation models are at work.\( ^{30} \)

Having established the typical behavior of the density of states at the Dirac point due to midgap states, we will discuss several scattering mechanisms.

**IV. RELAXATION TIME AND DC CONDUCTIVITY**

The collision rate \( 1/\tau_k \) due to impurity scattering is usually given by\( ^{28} \)

\[
\frac{1}{\tau_k} = N_i \sum_{k'} \Gamma(k, k')(1 - \cos \theta_{k,k'}),
\]

where \( N_i \) is the number of impurities and the transition rate from the quantum state \( k \) to \( k' \) is approximated by Fermi’s Golden rule

\[
\Gamma(k, k') = \frac{2\pi}{\hbar} |\langle k | V_{\text{scatt}} | k' \rangle|^2 \delta(E_k - E_{k'}) \text{.}
\]

It is only in the scattering matrix \( \Gamma(k, k') \), where the chirality of the Dirac fermions enters within the Boltzmann formalism. If the scattering potential does not break the sub-lattice symmetry, this will only lead to a numerical
factor. With the Fourier transform of the scattering potential $V_{\text{scatt}}(q)$, the collision rate can then be written as
\begin{equation}
\frac{\hbar}{\tau_{kF}} = \frac{n_{i}^{\text{scatt}}}{8} \rho(E_F) \int d\theta |V_{\text{scatt}}(q)|^2 (1 - \cos^2 \theta),
\end{equation}
where $n_{i}^{\text{scatt}}$ is the impurities density of the scattering potential and $q = 2k_F \sin(\theta/2)$. Notice that the argument of the integral vanishes for both $\theta = 0$ and $\theta = \pi$, a situation that does not occur in normal metals.

The effect of vacancies or local impurities with a high potential difference with respect to the graphene layer cannot be treated with the above formulas since they do not capture the change in phase space due to midgap states. We thus determine the relaxation time via the phase shift induced by the scattering center. Assuming elastic scattering and only considering s-wave scattering, the transition-rate is then expressed as
\begin{equation}
\frac{\hbar}{\tau_k} = \frac{8n_i}{\pi \rho(E_k)} \sin^2(\delta_k)
\end{equation}
where $\delta_k$ is the phase-shift of the s-wave channel.

In the following, we will consider various scattering mechanisms, i.e., we will discuss the effect on the electronic conductivity due to a) local substitutions (short-range “contact” potential); b) charged impurities in the SiO$_2$ substrate (long-range (screened) Coulomb-potential); c) acoustic phonons, where Eqs. (20) and (21) have to slightly be modified. In Subsection IV D we introduce the new scattering mechanism due to midgap states.

Due to the unusually high energies of optical phonons of the order of 0.1-0.2 eV in graphene-related materials, optical phonons cannot be treated within the Boltzmann- formalism since they induce interband-transitions for usual densities $n \lesssim 5 \times 10^{12}$ cm$^{-2}$. For a discussion on transversal optical phonons in graphene sheets within the Kubo-formalism, see Ref. 25.

A. Contact potential

We will first discuss the scattering behavior from $V_{\text{scatt}}(r) = v_0 \delta(|r|)$. This yields a relaxation time
\begin{equation}
\tau_k = \frac{8\hbar}{n_i^{\text{Contact}}} \frac{1}{\pi v_0^2} \rho(E_k) \rightarrow \frac{4\hbar^2 v_F k_F^2}{n_i^{\text{Contact}} v_0^2 E_k}
\end{equation}
where $n_i^{\text{Contact}}$ is the impurity concentration and the right hand side resembles the high carrier density limit.

Eq. (23) can also be obtained from calculating the phase shifts. From Ref. 20 we obtain $\delta_k = v_0 k/(4v_F)k_F$ in the limit of small $k$ and by expanding Eq. (23) up to linear order in $\delta_k$, we obtain the above result.

The conductivity does not depend on doping and we obtain
\begin{equation}
\sigma_{\text{Contact}} = \sigma_{\text{min}} = \frac{8e^2}{\hbar} \frac{(hv_F k_F)^2}{n_i^{\text{Contact}} v_0^2},
\end{equation}
Eq. (25) does not depend on an energy scale nor does it lead to a significant contribution for the total conductivity. This is more generally known as the Klein-paradox.

B. Long-range Coulomb potential

Let us now discuss the influence of the long-range Coulomb potential. Charged impurities reside in the isolating SiO$_2$ layer and are screened by the conduction electrons of the graphene sheet. This yields for the potential in momentum space
\begin{equation}
\varphi(q) = \frac{1}{2e\hbar q} \rho^{\text{ind}}(q) + \frac{Ze}{2e\hbar q} e^{-qz_c}
\end{equation}
where $\rho^{\text{ind}}(q)$ is the induced charge density, $\epsilon$ the permeability of the substrate, and $z_c$ denotes the shortest distance of the external charged impurity to the two-dimensional graphene sheet.

Since we are employing a semi-classical approach, it is consistent to approximate the induced charge density within the Thomas-Fermi (TF) approach:
\begin{equation}
\rho^{\text{ind}}(r) = -e^4 \sum_k \left( f(\epsilon_k - e\varphi(r)) - f(\epsilon_k) \right)
\approx -e^2 \varphi(r) \sum_k \left( \frac{\partial f(\epsilon_k)}{\partial \epsilon_k} \right) = -e^2 \varphi(r) \rho_F
\end{equation}
The last equality follows by assuming a Fermi liquid characterized by a sharp Fermi “surface”. For a discussion on non-linear screening, see Ref. 35.

The TF approach thus gives the following form for the screened potential inside the graphene sheet:
\begin{equation}
\varphi(q) = \frac{Ze}{2e\hbar q} e^{-qz_c},
\end{equation}
with $\gamma = \rho(E_F)e^2/2e\hbar q$ and the density of states given by Eq. (17).

At large doping we have $\gamma = \gamma k_F$ and from Eq. (22) with $V_{\text{scatt}}(q) = e\varphi(q)$ and $z_c \approx 0$ we obtain
\begin{equation}
\tau_{kF} = \frac{\hbar^2 v_F k_F^2}{u_0^2}, \text{ with } u_0 = \sqrt{n_i^C Ze^2} / 4e\hbar (1 + \gamma)
\end{equation}
where $n_i^C$ is the density of charged impurities in the sample. This leads to the following conductivity:
\begin{equation}
\sigma^{\text{Coulomb}} = \frac{2e^2}{\hbar} \frac{(hv_F k_F)^2}{u_0^2}
\end{equation}
Eqs. (29) and (30) are slightly modified for $z_c > 0$.

At zero doping, we obtain the minimal conductivity
\begin{equation}
\sigma^{\text{Coulomb}}_{\text{min}} = \frac{4e^2}{\hbar} \frac{n_i}{n_i^C (2\alpha)^2}.
\end{equation}
We thus find universal behavior at low doping if \( n_i \approx n_i^C \). For \( \alpha = 1/2 \), we obtain the the experimentally observed value of \( \sigma = 4e^2/h \).

Now we want to determine the numerical values of the relaxation times due to charged impurities and later compare them to the ones due to acoustic phonon scattering. Let us assume that the electronic density in the graphene sample, induced by the gate voltage, has the typical value (gate voltage of 100 V
\[ n = 7.2 \times 10^{12} \text{ cm}^{-2}. \] (32)

The Fermi momentum is given by \( n = k_F^2/\pi \), where contributions from both spins and both Dirac points were included; this leads to a value for \( k_F \) given by
\[ k_F = 4.8 \times 10^8 \text{ m}^{-1}. \] (33)

With \( e^2/4\pi\varepsilon_0 = 14.4\text{eVÅ} \) and \( \hbar v_F = 3at/2 = 5.75\text{eVÅ} \) where \( a = 1.42\text{Å} \) and \( t = 2.7\text{eV} \), we find for large densities \( \gamma = 10k_F/\epsilon \). For \( Z = 1 \) and \( z_c \approx 0 \) we set \( \epsilon = 2.4 \) which is the average of the dielectric constant of SiO\(_2\) and vacuum, since the graphene-layer is sandwiched by these two layers. For large carrier densities, we thus have \( \gamma = \gamma k_F \) with \( \gamma \approx 4.2 \).

Using Eq. (29) and the above value for \( k_F \) we obtain
\[ \tau_{k_F} \approx 6 \times 10^{-17}(n_i^C)^{-1} \text{ s}, \] (34)
where \( n_i^C \) is the concentration of impurities per unit cell. Since it has been experimentally determined that the mean free path \( \ell \) of electrons in graphene can be as large as 0.3 \( \mu \text{m} \) the experimental relaxation time is seen to be of the order of
\[ \tau \approx \frac{\ell}{v_F} \approx 3 \times 10^{-13} \text{ s}. \] (35)

This last result implies that the concentration of impurities per unit cell has a value of the order of
\[ n_i^C \approx 2 \times 10^{-4}, \] (36)
if one only assumes the Coulomb scattering mechanism. This corresponded to a density of \( n_i^C \approx 4 \times 10^{11} \text{cm}^{-2} \) and a mobility of 11100 \text{cm}^2/\text{Vs}. But note that graphene normally exhibits lower mobilities for which a higher impurity density is necessary. Also finite \( z_c \) and a higher dielectric constant, e.g. \( \epsilon = 3.9 \) which holds for SiO\(_2\), lead to a larger relaxation time and thus imply higher impurity concentrations to match the experimental results. In summary, we strongly believe that the Coulomb scattering mechanism is only capable to explain a marginal fraction of the observed data.

### C. Phonons

The relaxation time \( \tau_k \) for phonon scattering is defined as
\[ \frac{1}{\tau_k} = \sum_k \Gamma(k, k')(1 - \cos \theta), \] (37)
where the transition rate \( \Gamma(k, k') \) is given by
\[ \Gamma(k, k') = \frac{2\pi}{\hbar} |H_{k, k'}|^2 \delta(v_F h k' - v_F h k - \hbar \omega), \] (38)
where \( v_F h k \) is the dispersion of Dirac fermions in graphene, \( \hbar \omega \) the phonon energy and \( H_{k, k'} \) is defined as
\[ H_{k, k'} = \int dr \psi_k^*(r) U_S(r) \psi_k(r), \] (39)
with \( U_S(r) \) the scattering potential and \( \psi_k(r) \) is the electronic wave function of a clean graphene sheet.

If the potential is due to the propagation of phonons it has the form
\[ U_S = K_q A_q e^{i(q \cdot r - \omega t)} \] (40)
where
\[ |K_q|^2 = D_A^2 q^2, \] (41)
\[ |A_q|^2 = \frac{\hbar}{2\rho A \omega_q} N(\omega_q), \] (42)
\[ N(\omega_q) = \frac{1}{e^{\hbar \omega_q/(k_B T)} - 1} \approx \frac{k_B T}{\hbar \omega_q}, \] (43)
where \( \rho \) is the density of graphene and \( D_A \) is the electron acoustic deformation potential, estimated to be of the order of \( 3t \), where \( t \) is the first neighbor hopping matrix in graphene of the order of \( 3 \text{ eV} \). A similar estimate for the deformation potential is obtained by relating the bond-length with the hopping amplitude.

The matrix element \( H_{k, k'} \) is easily obtained as
\[ H_{k, k'} = \cos(\theta/2) K_q A_q \delta_{k+q, k'} e^{-i\omega t}. \] (44)

Using Eq. (34) in Eq. (38), the transition rate \( \Gamma(k, k') \) reads
\[ \Gamma(k, k') = \frac{\pi}{\hbar} |K_q|^2 |A_q|^2 (1 + \cos \theta) \delta_{k+q, k'} \times \delta(v_F h k' - v_F h k - \hbar \omega_q). \] (45)

The form of \( \Gamma(k, k') \) represents the absorption of a phonon of momentum \( q \) and energy \( \hbar \omega_q \). Since we want to describe the absorption of acoustic phonons, we write the dispersion \( \omega_q \) as
\[ \omega_q = v_S q, \] (46)
where \( v_S \) is the sound velocity. The conservation of momentum, \( k + q = k' \), leads to
\[ q = \sqrt{k'^2 + k^2 - 2k'k \cos \theta}, \] (47)
which allows us to write the product of the Kronecker symbol and the Dirac delta function as a single delta function reading
\[ \delta(v_F h k' - v_F h k - \hbar v_S \sqrt{k'^2 + k^2 - 2k'k \cos \theta}). \] (48)
Since \( v_F \gg v_i \), the argument of the delta function \( \frac{h}{2} k R \) can be approximated by \( v_F h k' - v_F h k \), i.e., the absorption of acoustic phonons can be seen as a quasi-elastic scattering process.

The final result for the scattering time is
\[
\tau_k \approx \frac{8h^2 \rho e^2 v_F}{D_2^2 k_B T} k, \tag{49}
\]
which is formally similar to the relaxation time produced by a contact potential, Eq. (23), except for the temperature dependence which is absent in the latter case.

Let us now concentrate on the numerical values of the relaxation time due to phonons. The phonon spectrum of graphene has two acoustic branches named \( LA \), with a velocity of \( 7.33 \times 10^4 \) m/s, and \( TA \), with a velocity of \( 2.82 \times 10^3 \) m/s\(^2\). At the temperature of 1 K the relaxation times of these two modes are
\[
\tau_{LA} \approx 2.7 \times 10^{-10} \text{ s}, \tag{50}
\]
\[
\tau_{TA} \approx 4.0 \times 10^{-11} \text{ s}, \tag{51}
\]
which are clearly much larger than the estimated value of \( 3 \times 10^{-13} \) s. Therefore at this low temperatures the scattering is mainly dominated by impurities. At temperatures around 100 K the scattering life time diminishes by a factor of 100 leading to values comparable to that obtained from the scattering from charged impurities. Considering only charged impurities as scattering mechanism, the effect of phonons on the transport properties of graphene must be taken into account if the calculations of the transport coefficients are extended to temperatures of the order or above 100 K.

Let us finally discuss the effect of temperature on the need of taking into account thermal excitations of the valence band into the conduction band. For the value of the Fermi momentum given above the Fermi energy has a value of \( h v_F k_F = 0.3 \) eV. This energy value corresponds to a temperature of the order of 3600 K. Therefore as long as the temperature is much smaller than this value the valence band can be considered as inert and therefore we can perform the calculations by neglecting the effect of the valence band altogether.

### D. Vacancies

Vacancies, cracks or boundaries in the graphene sheet give rise to bound states at the Dirac point, so-called midgap states. This is also true for corrugated graphene. There is thus inherent disorder in the system that has to be treated adequately. The influence of midgap states is not captured in Eqs. (20) and (21), where the reference point is given by the unperturbed system described by plane (spinor) waves, i.e., \( \psi_k(x) = (\mathbf{k}|k) \) is the electronic wave function of a clean graphene sheet. This is also the reason why the Klein paradox is not at work which would render scattering from local impurities (i.e., vacancies) irrelevant.

In order to incorporate the effect of midgap states in the calculation of the relaxation time we depart from Eq. (23). Scattering from vacancies leads to the following phase-shift\(^20\).

\[
\delta_k = \frac{\pi}{2} \frac{1}{\ln(k R_0)} \tag{52}
\]

This means that for \( k R_0 \ll 1 \)
\[
\tau_k = \frac{k \rho(E_k)}{2 \pi \nu_i (\ln(k R_0))^2}. \tag{53}
\]

For large carrier densities, \( \rho(E_k) \sim k \), and apart from the logarithmic correction, this is the scattering behavior coming from long-range Coulomb potentials\(^20,27\). Explicitly, one obtains
\[
\tau_k = \frac{k}{\pi v_F \nu_i} (\ln(k R_0))^2. \tag{54}
\]

The logarithmic correction leads to a sub-linear density dependence of the conductivity
\[
\sigma_{\text{Vacancies}} = \frac{e^2}{\hbar} \frac{2}{\pi} k_F^2 (\ln(k R_0))^2. \tag{55}
\]

We note that the same behavior is obtained if one includes wiggles and thus a random magnetic field in the graphene sheet\(^22\). The relation between midgap states and corrugated graphene was investigated in Ref.\(^19\).

For zero carrier density, we obtain with \( k_{\text{min}} \sim n_i^{1/2} \) the following result for the minimal conductivity \( \sigma_{\text{min}} \approx \sigma_c \) and \( R_0^2 \sim A_c \):
\[
\sigma_{\text{Vacancies}}^{\text{min}} = \frac{e^2}{\hbar} (\alpha |\ln(n_i)|)^2 \tag{56}
\]

Notice that there is no “linear” dependence of the impurity density \( n_i \). Having a typical impurity density per unit cell of \( n_i = 10^{-4} \) which matches well the experimentally observed mobility, the logarithmic correction can be approximated as \( |\ln(n_i)| \approx 8 \). For \( \alpha = 1/4 \), we obtain the experimentally observed minimal conductivity \( \sigma_{\text{min}} \approx 4 e^2/\hbar \).

For cleaner samples the logarithmic correction has to be taken into account. This is in accordance to experimental findings which show higher conductivity for cleaner samples\(^14,42\).

### V. OTHER TRANSPORT QUANTITIES

In Ref.\(^22\), predictions were made on how the ac conductivity, the thermal conductivity and the thermopower depend on the carrier density if one assumes the scattering behavior \( \tau_k \sim k \). The scattering mechanism from vacancies, cracks or boundaries yields a different scattering behavior, i.e., \( \tau_k \sim k (\ln(k R_0))^2 \). In the following we give the density dependence in terms of the Fermi energy \( E_F = h v_F k_F \) for the above quantities assuming this new scattering mechanism at work \( (n = E_F^2/\pi) \). Measuring these quantities may then disclose which scattering mechanism dominates.
A. The optical conductivity

Here we want to obtain the electronic density dependence of the optical conductivity of a doped graphene plane. Since the Boltzmann approach does not include inter-band transitions, the expressions obtained below are only valid as long as \( h\omega \leq E_F \) with \( E_F = h v_F k_F \) the Fermi energy, where the above mentioned transitions are blocked by the Pauli principle.

Our aim is to obtain the response of the electronic system to an external electric field of the form

\[
E = E_0 e^{i(q \cdot r - \omega t)}. \tag{57}
\]

The Boltzmann equation has, for this problem, the form

\[
-\frac{\partial f^0(\epsilon_k)}{\partial \epsilon_k} v_k \cdot E = \frac{g_k}{\tau_k} + v_k \cdot \nabla_r g_k + \frac{\partial g_k}{\partial t}. \tag{58}
\]

The solution of the linearized Boltzmann equation \((58)\) is well known, reading

\[
g_k = -\frac{\partial f^0(\epsilon_k)}{\partial \epsilon_k} \Phi_q(\omega, k)e^{i(q \cdot r - \omega t)}, \tag{59}
\]

with

\[
\Phi_q(\omega, k) = \frac{e\tau_k v_k \cdot E_0}{1 - i\omega\tau_k + i\tau_k q \cdot v_k}. \tag{60}
\]

The Fourier component \( J(\omega, q) \) of the current is given by

\[
J(\omega, q) = \frac{1}{\pi^2} \int d^2 k e^2 \Phi_q(\omega, k) \left(-\frac{\partial f^0(\epsilon_k)}{\partial \epsilon_k} \right), \tag{61}
\]

leading in the long-wavelength limit to an optical conductivity of the form

\[
\sigma(\omega) = 2\frac{e^2}{\hbar} \frac{E_0^2}{\bar{v}_0^2} \frac{1 + i\omega\tau_F}{1 + (\frac{\omega\tau_F}{\bar{v}_0})^2} (\ln E_F/\bar{v}_0)^2. \tag{62}
\]

In the above equation, we defined the two energy scales \( \bar{v}_0^2 = \pi^2 n_i \hbar^2 v_F^2 \) and \( \bar{v}_0 = h v_F/R_0 \). What should be stressed about Eq. \((62)\) is its density dependence \( n = E_F^2/\pi \).

B. Thermal conductivity and thermopower

In the presence of a temperature gradient in the sample, the linearized Boltzmann equation has the form

\[
-\frac{\partial f^0(\epsilon_k)}{\partial \epsilon_k} v_k \cdot \left(-\frac{\epsilon_k - E_F}{T}\right) \nabla_r T + eE_{\text{observ.}} = \frac{g_k}{\tau_k}, \tag{63}
\]

where the measured electric field is given by \( E_{\text{observ.}} = E - \nabla_r E_F/e \). In this situation we have, in addition to the electric current, a heat current (flux of heat per unit of area) given by

\[
U = \frac{4}{A} \sum_k v_k (\epsilon_k - E_F) g_k. \tag{64}
\]

Both the electric and the heat currents can be written as

\[
J = e^2 K_0 \cdot E_{\text{observ.}} + \frac{e}{T} K_1 \cdot (-\nabla_r T) \tag{65}
\]

\[
U = eK_1 \cdot E_{\text{observ.}} + \frac{1}{T} K_2 \cdot (-\nabla_r T),
\]

where \( K_i, i = 0, 1, 2 \) are second order tensors. In this problem the tensors are diagonal, i.e. \( K_i = k_i \), and by a well established procedure one obtains

\[
k_0 = 2 \frac{E_F^2}{\hbar} \frac{E_F}{\bar{v}_0} (\ln E_F/\bar{v}_0)^2, \tag{66}
\]

\[
k_1 = \frac{4\pi^2}{3} \frac{k_B T}{\hbar} \frac{E_F}{\bar{v}_0} (\ln E_F/\bar{v}_0)^2 \left(1 + (\ln E_F/\bar{v}_0)^{-1}\right), \tag{67}
\]

\[
k_2 = 2 \frac{\pi^2}{3} \frac{k_B T}{\hbar} \frac{E_F^2}{\bar{v}_0} (\ln E_F/\bar{v}_0)^2. \tag{68}
\]

In the above equations, we defined the two energy scales \( \bar{v}_0^2 = \pi^2 n_i \hbar^2 v_F^2 \) and \( \bar{v}_0 = h v_F/R_0 \).

From the results \((66), (67)\) and \((68)\) it is easy to derive both the thermal conductivity \( \kappa \) and the thermopower \( Q \). These are given by

\[
\kappa = \frac{1}{T} \frac{2\pi^2}{3} \frac{k_B T}{\hbar} \frac{E_F^2}{\bar{v}_0} (\ln E_F/\bar{v}_0)^2 \tag{69}
\]

\[
-\frac{8\pi^4}{9} \frac{k_B T}{\hbar} \frac{1}{\bar{v}_0} (1 + \ln E_F/\bar{v}_0)
\]

and

\[
Q = \frac{1}{eT} \frac{2\pi^2}{3} \frac{k_B T}{E_F} (k_B T)^2 \left(1 + (\ln E_F/\bar{v}_0)^{-1}\right). \tag{70}
\]

Again, what should be emphasized in these results is the dependence of both \( \kappa \) and \( Q \) on the particle density, which is different from that of the usual two dimensional electron gas and from the graphene sheet with only charged impurities in the substrate. Since it is experimentally feasible to control the carrier density in the graphene plane, it is possible to check experimentally the dependence of the transport coefficients on the particle density. Finding the logarithmic corrections compared to the Coulomb scattering mechanism will be a strong indication for scattering due to midgap states.

Normally, the second term of Eq. \((69)\) can safely be neglected and one obtains the well-known Wiedemann-Franz law

\[
\kappa = \frac{\pi^2 k_B^2}{3} \frac{T}{e^2 \sigma}. \tag{71}
\]
at finite temperatures including scattering from charged impurities. Since there are two different mechanisms the total relaxation times is
\[
\frac{1}{\tau_{kF}} = \frac{u_0^2}{v_F \hbar^2 k_F} + \frac{D^2 k_B T}{8 \hbar^2 v_F^2 v_F} k_F = \frac{\alpha_1}{k_F} + \alpha_2 k_F ,
\] (72)
where \( u_0 \) was defined in Eq. (29) with \( Z = 1, \epsilon = 2.4 \) and \( \gamma = 4.2 \).

The conductivity, including the contribution from two Dirac cones, reads
\[
\sigma = 2e^2 \frac{E_F^2}{\hbar} k_F \int_0^\infty \frac{x^2 dx}{\alpha_1 + \alpha_2 k_F^2 x^2} \cosh^{-2} \left( \frac{E_F x - \mu}{2 k_B T} \right),
\] (73)
where \( E_F = v_F \hbar k_F \). The integral has a maximum around \( x = 1 \) and can be done numerically. The chemical potential depends on the temperature and in the temperature range of \( T \in [1, 300] K \) is well described by the asymptotic expression
\[
\mu \simeq \epsilon_F - \frac{(\pi k_B T)^2}{6 E_F}.
\] (74)

In Fig. 1 the conductivity as function of the electronic density is shown for different values of temperature and for two impurity concentrations \( \bar{n}_i = 2 \times 10^{-4} \) (left hand side) and \( \bar{n}_i = 2 \times 10^{-3} \) (right hand side). In Fig. 2 the conductivity as function of temperature is shown, for two impurity concentrations \( \bar{n}_i = 2 \times 10^{-3} \) (upper panels) and \( \bar{n}_i = 2 \times 10^{-4} \) (lower panels), and for two different electronic densities \( n = 7.2 \times 10^{12} \text{cm}^{-2} \) (left hand side) and \( n = 1.2 \times 10^{12} \text{cm}^{-2} \) (right hand side).

For low impurity density, i.e., for realistic parameters, there is a striking temperature effect on the conductivity which is not seen in experiment. We, therefore, conclude once again that charged impurity can not resemble the main scattering mechanism.

VI. NUMERICAL RESULTS

A. Phonon contribution

We now use the obtained values for the relaxation times of phonon scattering to compute the conductivity at finite temperatures including scattering from charged impurities. Since there are two different mechanisms the total relaxation times is
\[
\frac{1}{\tau_{kF}} = \frac{u_0^2}{v_F \hbar^2 k_F} + \frac{D^2 k_B T}{8 \hbar^2 v_F^2 v_F} k_F = \frac{\alpha_1}{k_F} + \alpha_2 k_F ,
\] (72)
where \( u_0 \) was defined in Eq. (29) with \( Z = 1, \epsilon = 2.4 \) and \( \gamma = 4.2 \).

The conductivity, including the contribution from two Dirac cones, reads
\[
\sigma = 2e^2 \frac{E_F^2}{\hbar} k_F \int_0^\infty \frac{x^2 dx}{\alpha_1 + \alpha_2 k_F^2 x^2} \cosh^{-2} \left( \frac{E_F x - \mu}{2 k_B T} \right),
\] (73)
where \( E_F = v_F \hbar k_F \). The integral has a maximum around \( x = 1 \) and can be done numerically. The chemical potential depends on the temperature and in the temperature range of \( T \in [1, 300] K \) is well described by the asymptotic expression
\[
\mu \simeq \epsilon_F - \frac{(\pi k_B T)^2}{6 E_F}.
\] (74)
states can also occur from cracks or boundaries. Another realization comes from impurities with large potential difference with respect to the graphene sheet or corrugated graphene. We summarize all these effects in the impurity density for a carrier density $n = 7.2 \times 10^{12}\text{cm}^{-2}$ (dotted line).

FIG. 3: (color online). The mobility $\mu$ in units of cm$^2$/Vs due to Coulomb scatterers with $\epsilon = 3.9$, $2.4$; $z = 5\text{nm}$ and $\epsilon = 2.4$; $z = 0$ (solid lines), and vacancies as function of the impurity density for a carrier density $n = 7.2 \times 10^{12}\text{cm}^{-2}$ (dotted line).

The conductivity of the cleaner sample (left hand side) is not affected by the Coulomb scattering mechanism and shows sub-linear behavior in the electronic density. For the dirty sample (right hand side) with $z_c = 5\text{nm}$, i.e., the charged impurities are well inside the substrate, the Coulomb scattering mechanism leads to super-linear behavior which in total yields linear behavior of the combined conductivity with respect to the carrier density $n$. The above parameters yield mobilities of $\mu \approx 12000\text{cm}^2/\text{Vs}$ (left) and $\mu \approx 8800\text{cm}^2/\text{Vs}$ (right).

VI. CONCLUSIONS

In summary, we presented a phenomenological theory for transport in graphene based on the semi-classical Boltzmann theory, first proposed by Nomura and MacDonald. We pointed out that local point defects in form of vacancies, cracks etc. yield a similar $k$-dependence of the relaxation time as long-range Coulomb potentials. Moreover, they lead to a finite density of states at the Dirac point which can account for the observed minimal conductivity. The scattering mechanism due to midgap states has been widely ignored so far, but actually represents the dominant contribution to the total conductivity.

For “dirty” samples, this scattering mechanism yields an universal minimal conductivity, whereas for “cleaner” samples, the minimal conductivity increases. It also leads to a sub-linear behavior with respect to the carrier density. In combination with Coulomb scattering, this behavior may become linear.

Regarding the numerical values, the major uncertainty lies in the impurities densities of charged or neutral defects. Cleaning the SiO$_2$ surface in a hydroxyl bath\cite{44,45} would reduce charged impurities close to the graphene sheet and thus estimate their effect to the conductivity. Another way of reducing a possible source of impurities is by interchanging the mechanical cleavage by “printing” the graphene sheet on top of the substrate.\cite{46}

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