Optical properties of graphene

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Abstract. Reflectance and transmittance of graphene in the optical region are analyzed as a function of frequency, temperature, and carrier density. We show that the optical graphene properties are determined by the direct interband electron transitions. The real part of the dynamic conductivity in doped graphene at low temperatures takes the universal constant value, whereas the imaginary part is logarithmically divergent at the threshold of interband transitions. The graphene transmittance in the visible range is independent of frequency and takes the universal value given by the fine structure constant.

1. Introduction
Monolayer and bilayer graphenes are gapless two-dimensional (2D) semiconductors whereas its 3D relative, graphite, is a semimetal. Hence the dimensionality effects can be studied in the unique substance. Graphene has a very simple electron band structure. Near the energy \( \varepsilon = 0 \), the energy bands are cones \( \varepsilon_{1,2}(p) = \pm vp \) at the \( K \) points in the 2D Brillouin zone with the constant velocity parameter \( v = 10^8 \text{ cm/s} \). Such a degeneration is conditioned by symmetry because the small group \( C_{3v} \) of the \( K \) points has a two-dimensional representation.

While the carrier concentration is decreasing in the field gate experiment, the graphene conductivity at low temperatures goes to the finite minimal value. Much theoretical efforts have been devoted to evaluate the minimal conductivity within different approaches. Theoretical and experimental researches show that the main mechanism of the carrier relaxation is provided by the long range scatterers and gives the collision rate \( \tau^{-1} \approx 2\pi^2\epsilon^4n_{imp}/\hbar\epsilon_g^2\varepsilon \), where \( \epsilon_g \) is the dielectric constant of graphene, \( \varepsilon \) is the characteristic electron energy (of the order of the Fermi energy or temperature), and \( n_{imp} \) is the density of scatterers per the unit surface.

The general quantum expression for the conductivity depending on the frequency \( \omega \) and the wave vector \( k \) has been derived in our paper [1]. In various limiting cases, our result coincides with the formulas of Refs. [2, 3]. This expression is valid if the collision rate of carriers is much less than frequency and spatial dispersion, \( \tau^{-1} \ll \omega, kv \). In the optical region, we can neglect the spatial dispersion of conductivity compared with the frequency dependence and use the dynamical conductivity \( \sigma(\omega) \) to study the graphene optical properties [4]. The optical visibility of both monolayer and bilayer graphene was theoretically studied in Ref. [5] focusing on the role of the underlying substrate. Recently, graphene transmittance spectra were observed [6] and the dynamical conductivity was found as \( \sigma(\omega) = \epsilon^2/4\hbar \) in agreement with the theory.

In the present paper, we analyze in detail the optical properties of graphene and multilayer graphene. We use the dynamic conductivity \( \sigma \) as a function of frequency \( \omega \), temperature \( T \), and chemical potential \( \mu \). The chemical potential of pristine graphene at arbitrary temperatures
coincides with the crossing at \( \varepsilon = 0 \) of the bands \( \varepsilon_{1,2}(p) \). With the help of the gate voltage, one can control the density and type (n or p) of carriers varying their chemical potential. Using the dynamic conductivity and the appropriate boundary conditions at interfaces, we calculate the reflection and transmission coefficients of graphene and multilayer graphene with various carrier concentrations.

2. Optical conductivity of graphene

The general expression for conductivity used here is obtained in the previous paper [1]. For high frequencies, \( \omega \gg (kv, \tau^{-1}) \), the dynamical conductivity (see Eq. (8) in Ref. [1]) can be written as

\[
\sigma(\omega) = \frac{e^2}{i\pi\hbar} \left[ \int_{-\infty}^{+\infty} \frac{d\varepsilon}{\omega^2} |f_0(\varepsilon)| \, d\varepsilon - \int_{0}^{+\infty} \frac{d\varepsilon}{(\omega + i\delta)^2} \right],
\]

where \( f_0(\varepsilon) = \{\exp[(\varepsilon - \mu)/T] + 1\}^{-1} \) is the Fermi function.

The first term in Eq. (1) corresponds to the intraband electron–photon scattering processes. Integrating, we obtain explicitly:

\[
\sigma_{\text{intra}}(\omega) = \frac{2ie^2T}{\pi\hbar(\omega + i\tau^{-1})} \ln \left[ 2 \cosh(\mu/2T) \right].
\]

Here, we write \( \omega + i\tau^{-1} \) instead of \( \omega \) in order to take the electron–disorder scattering processes into account. In such a form, the intraband conductivity coincides with the Boltzmann-Drude expression. For the Fermi-Dirac statistics, \( \mu \gg T \), the intraband conductivity takes the form

\[
\sigma_{\text{intra}}(\omega) = \frac{ie^2|\mu|}{\pi\hbar(\omega + i\tau^{-1})},
\]

where the chemical potential is determined by the carrier concentration \( n_0 = (\mu/\hbar v)^2/\pi \).

The second term in Eq. (1) owes its origin to the direct interband electron transitions. The infinitesimal quantity, \( \delta \to 0 \), determines the bypass around the integrand pole. The integral is easily evaluated in the case of zero temperature:

\[
\sigma_{\text{inter}}(\omega) = \frac{e^2}{4\hbar} \left[ \theta(\omega - 2\mu) - \frac{i}{2\pi} \ln \left( \frac{\omega + 2\mu}{\omega - 2\mu} \right) \right].
\]

Here and below, we consider for simplicity the case of the positive \( \mu \). The step function \( \theta(\omega - 2\mu) \) conveys the condition for the interband electron absorption at low temperatures. The expression shows that the interband contribution plays the leading role at the absorption threshold, \( \omega \approx 2\mu \), in comparison with the Boltzmann-Drude intraband term, Eqs. (2) and (3), which is important at relatively low frequencies, \( \omega < \mu \). The logarithmic singularity is cut off with the temperature. At the finite, but low temperatures, the following substitutions should be made in Eq. (4)

\[
\theta(\omega - 2\mu) \to \frac{1}{2} + \frac{1}{\pi} \arctan[(\omega - 2\mu)/2T],
\]

\[
(\omega - 2\mu)^2 \to (\omega - 2\mu)^2 + (2T)^2.
\]

The electron relaxation processes produce the similar smearing.

It is useful for numerical calculations to present the difference of the Fermi functions in the second integrand (1) as

\[
G(\varepsilon) = \frac{\sinh(\varepsilon/T)}{\cosh(\mu/T) + \cosh(\varepsilon/T)}.
\]
Adding and subtracting $G(\omega/2)$ in the numerator of integrand, and noticing that the principal value of the integral with $G(\omega/2)$ equals to zero, we arrive at the integral without singularities. Then we can write the interband conductivity in the form available for numerical calculations:

$$\sigma_{\text{inter}}(\omega) = \frac{e^2}{4\hbar} \left[ G(\omega/2) - \frac{4\omega}{i\pi} \int_0^{+\infty} d\varepsilon \frac{G(\varepsilon) - G(\omega/2)}{\omega^2 - 4\varepsilon^2} \right].$$ (6)

For the Fermi-Dirac and Boltzmann carrier statistics, correspondingly, the first term is asymptotically given by

$$G(\omega/2) = \begin{cases} \theta(\omega - 2\mu), & \mu \gg T, \\ \tanh(\omega/4T), & \mu \ll T. \end{cases}$$ (7)

The conductivity calculated with the help of Eqs. (2), (6) is shown in Fig. 1. The step-function behavior of the real part (absorption) and the logarithmic singularity of the imaginary part are clearly seen at low temperatures. The transition from the Boltzmann statistics to the Fermi-Dirac statistics with the temperature increase is also evident.

By using the gate voltage, one can control the density of electrons ($n_0$) or holes ($-n_0$). Then the chemical potential is determined by the condition

$$n_0 = \frac{2}{\pi (\hbar v_F)^2} \int_0^{+\infty} \varepsilon [f_0(\varepsilon - \mu) - f_0(\varepsilon + \mu)] d\varepsilon.$$ (8)

From this expression and Fig. 2(a), one can see that the chemical potential goes to zero while the temperature increases.

### 3. Spectroscopy of graphene layers

In order to calculate the graphene reflectance, we apply Maxwell’s equations

$$\nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = \varepsilon_0 \frac{\omega^2}{c^2} \mathbf{E} + \frac{4\pi i \omega}{c^2} \mathbf{j},$$ (9)
where $\epsilon_0$ is the ion contribution into the dielectric constant and $j$ is the conductivity current. We consider the case of the $p$-polarization, when the field $E$ belongs to the $xz$ plane and the current $j$ has only the in-layer $x$ component (see Fig 2b).

### 3.1. Optics of a monolayer.

Let us consider the graphene monolayer at $z = 0$ with $\epsilon_0 = \epsilon_g$ deposited on the substrate ($z > 0$) with the dielectric constant $\epsilon_0 = \epsilon_s$ ($\epsilon_s = 1$ for suspended graphene). The ac field is given by the sum of incident and reflected waves in the vacuum, $z < 0$, and by the transmitted wave in the substrate. In the geometry considered, the current in graphene can be written in the form

$$j_x = \sigma(\omega) \delta(z) E_x.$$  \hfill (10)

Making use of the Fourier transforms with respect to the $x$ coordinate, $E \propto e^{i k_x x}$, we rewrite the Maxwell equations (9) as follows

$$ik_x dE_z/dz - d^2 E_x/dz^2 - \epsilon_0 \frac{\omega^2}{c^2} E_x = \frac{4\pi i \omega}{c^2} j_x,$$

$$ik_x dE_x/dz + (k_z^2 - \epsilon_0 \frac{\omega^2}{c^2}) E_z = 0.$$  \hfill (11)

The boundary conditions for these equations at $z = 0$ are the continuity of the field component $E_x$ and the jump of the electric-induction $z$ component at the sides of the monolayer:

$$\epsilon_s E_x|_{z=+0} - E_z|_{z=-0} = 4\pi \int_{-0}^{+0} \rho(\omega, k_x, z) dz.$$  \hfill (12)

The carrier density is connected to the current in Eq. (10) according to the continuity equation

$$\rho(\omega, k_x, z) = j_x(\omega, k_x, z) k_x/\omega.$$  

Substituting $E_z$ from the second Eq. (11) into (12), we find the second boundary condition

$$\frac{\epsilon_s}{k_s^2} \frac{dE_x}{dz}|_{z=+0} - \frac{1}{k_z^2} \frac{dE_z}{dz}|_{z=-0} = \frac{4\pi \sigma(\omega)}{i\omega} E_x|_{z=0},$$  \hfill (13)

where

$$k_s = \sqrt{\epsilon_s (\omega/c)^2 - k_x^2}, \quad k_z^2 = \sqrt{(\omega/c)^2 - k_x^2}.$$  

Using the boundary conditions, we find the reflection ($r$) and transmission ($t$) amplitudes

$$r = \frac{1 - C}{1 + C}, \quad t = \frac{2}{1 + C},$$  \hfill (14)

where $C = k_z^2 [(4\pi \sigma(\omega)/\omega) + (\epsilon_s/k_s)]$. The very simple results can be written for suspended graphene, when $\epsilon_s = 1$ and $k_s = k_z^2$.

Then, the coefficient $C$ is close to the unity,

$$C = 1 + 4\pi \sigma(\omega) \cos \theta/c,$$  \hfill (15)

where $\theta$ is the incidence angle. Therefore, Eqs. (14) yield for the reflected and transmitted amplitudes within the first order in $\sigma(\omega)$

$$r = -2\pi \sigma(\omega) \cos \theta/c, \quad t = 1 - 2\pi \sigma(\omega) \cos \theta/c.$$  \hfill (16)
Figure 3. (color online). Transmittance spectrum of graphene with carrier densities \( n_0 = 10^{10} \text{ cm}^{-2} \) (left) and \( n_0 = 10^{11} \text{ cm}^{-2} \) (right) versus frequency; normal incidence. For the carrier density \( n_0 = 10^{11} \text{ cm}^{-2} \), the chemical potential equals to 428, 389, and 294 K at 3, 100, and 200 K, correspondingly.

Figure 4. (color online). Transmittance and reflectance at normal incidence for a film with the multilayer graphene and the carrier density \( n_0 = 10^{10} \text{ cm}^{-2} \) in a layer; the distance between layers \( d = 3.35 \text{ Å} \), thickness of the plate is \( l = 100d \), temperatures are noted at curves.

The transmission coefficient \( |t|^2 \) calculated for normal incidence with the help of Eqs. (2),(6), and (14) is shown in Figs. 3 as a function of frequency, temperature, and carrier density. One can see that the deviation of the graphene transmittance from the unity is proportional to the dimensionless parameter \( e^2 \text{max}(T, \mu)/\hbar c \omega \), i.e., it is relatively large at the very low frequencies \( \omega \approx e^2 \text{max}(T, \mu)/\hbar c \), when the intraband conductivity plays the leading role. At higher frequencies, the interband transitions do play the leading role. Then, the transmittance does not depend on frequency, being controlled by the fine structure constant \( e^2/\hbar c \). For instance, at normal incidence and \( T \ll \mu < \omega/2 \), the transmission coefficient is given by

\[
|t|^2 = 1 - \frac{4\pi}{c} \text{Re} \sigma(\omega) = 1 - \pi \frac{e^2}{\hbar c},
\]

where the logarithmic terms is omitted since it contains the fine structure constant squared. As was found recently [6], the linear (in the fine structure constant) effect can be observed on graphene in the visible region.

Reflectance increases with temperature, because the carrier density increases. As the chemical potential decreases with temperature, the reflectance is not monotonic on temperature as seen clearly in Fig. 3.

3.2. Spectroscopy of graphene multilayers.

Let the multilayers cross the z axis at points \( z_n = nd \), where \( d \) is the distance between layers (see Fig. 2b). Such a system can be considered as a model of graphite since the distance \( d = 3.35 \text{ Å} \) in graphite is larger than the interatomic distance in the layer. So, we describe the carrier interaction in the presence of ac electric field with the help of self-consistent Maxwell’s equations (9). For the \( x \) component of the field \( E_x \), they give

\[
\left( \frac{d^2}{dz^2} + k_g^2 + 2k_g D \sum_n \delta(z - nd) \right) E_x = 0,
\]
where \( D = 2i\pi \sigma(\omega)k_g/\epsilon_g\omega \) and \( k_g = \sqrt{\epsilon_g(\omega/c)^2 - k^2_x} \). For the infinite number of layers, the solutions of Eq. (18) represent two Bloch states

\[
e_{1,2}(z) = e^{\pm ik_z nd}\{\sin k_g(z - nd) - e^{-ik_z d} \times \\
\sin k_g[z - (n + 1)d]\}, \quad nd < z < (n + 1)d
\]

with the quasi-momentum \( k_z \) determined from the dispersion equation

\[
\cos k_z d = \cos k_g d - D \sin k_g d.
\]

The dispersion equation describes the electric field excitations in the system. The quasi-momentum \( k_z \) can be restricted within the Brillouin half-zone \( 0 < k_z < \pi/d \), if the parameter \( D \) is real. In the general case, while taking the interband absorption into account, we fix the choice of the eigenfunctions in Eq. (19) by the condition \( \text{Im} k_z > 0 \) so that the solution \( e_1 \) decreases in the positive direction \( z \).

In the long-wave limit, \( k_z, k_g \ll 1/d \), the dispersion equation (20) can be simplified. In this case, the dielectric permittivity can be introduced not only in the normal \( z \) direction, \( \epsilon_{zz} = \epsilon_g \simeq 2.5 \), but in the tangential direction as well, namely,

\[
\epsilon_{xx} = \epsilon_g + 4\pi i \sigma(\omega)/\omega d,
\]

where \( \sigma(\omega) \) is the dynamic conductivity, Eq. (1), of one layer. Then the dispersion equation (20) takes the form

\[
k^2_x \epsilon_{xx} + k^2_z \epsilon_{zz} = (\omega/c)^2 \epsilon_{xx} \epsilon_{zz}.
\]

We see from this equation, that the weakly damped solutions (for normal incidence, \( k_x = 0 \)) exist, if the real part of the dielectric function \( \epsilon_{xx} \) is positive and larger than the imaginary part. According Eqs. (3) and (4), this condition is fulfilled just below the threshold of interband transitions. Due to these weakly damped waves, at low temperatures, the maximum in transmittance and the corresponding minimum in reflectance of the multilayer system appear below the threshold as shown in Fig. 4.

Calculations done for a film with multilayer graphene give the following result for the amplitude of the reflected and transmitted waves

\[
r = -1 + 2k_z \frac{(k_z + k^*_z)f - (k_z - k^*_z)f^{-1}}{(k_z + k^*_z)^2f - (k_z - k^*_z)^2f^{-1}},
\]

\[
t = \frac{4k_z k^*_z}{(k_z + k^*_z)^2f - (k_z - k^*_z)^2f^{-1}},
\]

where \( f = \exp(-ik_z d) \), \( k^*_z = (\omega/c)\cos \theta \), \( k_z \) is determined by the dispersion equation (22) at fixed values of \( \omega \) and \( k_x = (\omega/c)\sin \theta \).

At higher frequencies, \( \omega > 2\mu = 270 \text{ K} \) (in Fig. 4), after the downfall, the reflection coefficient corresponds with the interband absorption presented by the \( \theta \)—singularity in the real part of conductivity. In contrast to the monolayer, the effect of carriers in the multilayers is controlled by the large dimensionless factor \( (e^2/\hbar \epsilon_g \omega d) \) [see Eq. (21)] of the function varying rapidly at \( \omega \approx 2\mu \). It means that the interband absorption can be observed at relatively large frequencies. Notice that observations of the absorption threshold provide a direct method of carrier density characterization in graphene.
4. Plasmons in graphene

As known, plasmons in 3D metals have a spectrum with the quadratic dispersion and the gap. In 2D graphene with carriers, plasmons are the gapless excitations with the square-root dispersion \( \omega \propto \sqrt{k} \). Their dispersion \([1, 7]\) can be found using Eq. (13). For instance, outside suspended graphene, \( z \neq 0 \), solutions decreasing at \( \pm z \) have a form, correspondingly,

\[
E_x = A \exp (\mp \kappa z), \quad \kappa = \sqrt{k_x^2 - (\omega/c)^2}.
\]

Inserting this form into condition (13), we obtain:

\[
-2\pi i \kappa \sigma(\omega) = \omega. \tag{24}
\]

As one can see from Eqs. (2) and (4), this equation gives the real solution for \( \omega \) or \( \kappa \) only for that frequency interval where the intraband conductivity plays the leading role and the condition \( \omega \gg \tau^{-1} \) is fulfilled. Retaining only the intraband term, we get the plasmon dispersion in doped graphene in the form

\[
\omega^2 = \frac{8e^2 T \kappa}{\hbar} \ln [2 \cosh(\mu/2T)].
\]

Usually, the term with \( \omega^2/c^2 \) can be omitted in the expression for \( \kappa \), i.e., \( \kappa = |k_x| \).

Let us underline the peculiar dependence of the plasmon frequency on the carrier density at low temperatures: \( \omega \propto n_0^{1/4} \).

In conclusion, we have developed the detailed microscopic theory of the graphene monolayer and multilayers spectroscopy. We have shown that reflectance from the monolayer is determined for infra-red region by the intraband Drude-Boltzmann conductivity and for higher frequencies by the interband absorption. We have argued that at low temperatures and high carrier densities, the reflectance from multilayers has the sharp downfall with the subsequent plateau. These features are caused by the excitations of weakly damped waves in conditions of the direct interband electron transitions.

Acknowledgments

This work is supported by the Russian Foundation for Basic Research (grant No. 07-02-00571).

5. References

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