

First-principles modeling of electron-phonon scattering rates in graphene

Valery N. Mishchanka¹

1 Belarusian State University of Informatics and Radioelectronics, 6 P. Brovka Str., Minsk 220013, Republic of Belarus

Corresponding author: Valery N. Mishchanka (mishchenko@bsuir.by)

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Abstract

Graphene, which has a high mobility of charge carriers, which exceeds the mobility of charge carriers for all known materials, is currently considered as one of the most promising materials for the creation of new semiconductor devices. The results of modeling of electron scattering rates are presented for the acoustic and optical phonons in a single layer of graphene without a substrate for small values of energy, which do not exceed 1 eV. When modeling these rates, variants of both emission and absorption of phonons are considered. The obtained dependences of the charge carrier scattering rates will allow us to study the main characteristics of charge carrier transport in semiconductor structures containing graphene layers by modeling using the Monte Carlo method. Characteristics and parameters of graphene can be used to create new heterostructure devices with improved output characteristics.

Keywords

graphene, phonon, modelling, semiconductor structure

1. Introduction

Graphene is of great interest as a promising material for the development of new semiconductor devices for various frequency ranges [1–2]. The study of charge carrier transfer processes for semiconductor compounds containing graphene layers is an urgent task, which is associated with the development of fast and powerful devices in the microwave range, as well as in the optical frequency range. The Monte Carlo statistical method is widely used to analyze semiconductor structures. One of the main features of this method is that it allows to take into account the processes of charge carriers scattering in the semiconductor and to study the operation of semiconductor de-

vices in different operating conditions. In semiconductor structures the processes of electron-phonon interaction (EPI) occupy an important place, among which the main role is played by the processes of electron scattering on optical and acoustic phonons.

It is believed that EPI determines the main transport properties of charge carriers in metals [3, 4] and semiconductors [5–9] in a large temperature range, and also plays an important role in the course of other processes, including superconductivity [10, 11]. EPI is based on the exchange of energy and momentum between electrons and phonons, which determines the main transport parameters of charge carriers. Quasi-analytical dependences of electron-phonon (e-ph) coupling matrices for various scattering processes have been developed for

quantitative evaluation of EPI. They have been used to obtain scattering rates based on the Fermi golden rule and thus to describe the charge carrier transport properties [8, 9].

Bardeen and Shockley [5] first proposed a concept known as the deformation potential for EPIs in semiconductors. This concept allows us to determine the rates of the interaction of electrons with acoustic and optical phonons when the zone diagram shifts due to local deformation. Long-wavelength acoustic phonons generate a corresponding crystal broadening, and relative changes in the inter-atomic distance lead to a perturbed potential that tends to change the energy of the zone diagram and thus the inter-action with electrons. Herring and Vogt [6] generalized the strain-potential theory and calculated the relaxation time and mobility tensors of n-type silicon and germanium. Harrison [12] extended the deformation-potential theory to optical phonons for the case when the crystal lattice of a material has two or more atoms as a basis.

Based on the concept of deformation potential, a number of analytical expressions were proposed for graphene to estimate the scattering of electrons on optical and acoustic phonons [13–14]. However, the semi-empirical expressions obtained in this way have serious limitations for the study of EPIs because of the simplifications made in their derivation. The main simplification of these expressions is related to the necessity of selecting the value of strain potentials either from experimental measurements or from the calculated data of other theoretical approaches.

The limitations associated with the use of deformation potentials are largely removed by using density functional perturbation theory (DFPT) [15] and an interpolation scheme using Wannier functions [16]. This approach allows to fully determine the EPI coupling matrix from ab initio calculations (first-principles calculations) [17–18], without using empirical values of the strain potential. In [19], an ab initio analysis of EPI was performed for a single layer of graphene in a vacuum. To obtain the dependences of electron scattering intensities (velocities) on acoustic and optical phonons, the calculations of EPI matrix elements were initially performed using the Quantum Espresso software package [20], and then Fermi's golden rule was used. However, the obtained values of electron scattering rates on acoustic and optical phonons at small energy values were much lower than the values obtained earlier in [21, 22].

In this work, an ab initio study of the properties of EPIs associated with electron scattering on optical and acoustic phonons in graphene was carried out. Using Wannier functions, the coupling matrices of EPIs were calculated, which were then used to model the rates of electron scattering on acoustic and optical phonons. The obtained modeling results allow us to determine the contribution of various EPI components in the overall process of charge carrier scattering.

2. Method and peculiarities of modeling of electron-phonon scattering rates in graphene

First-principles simulations were performed with the Quantum Espresso [20] and EPW [23, 24] software packages using the Perdew–Burke–Ernzerhof (PBE) parameterization in the framework of the local density approximation (LDA). Self-consistent energy modeling and calculation of electron-phonon dynamical matrices were performed using the Quantum Espresso software package. During modeling in the Quantum Espresso software package, pseudopotentials of the Norm-conserving type [25] and the following modeling parameters were used: the cutoff energy of the wave function was 60 Ry (1 Ry $\approx$ 13.605 eV), the cutoff energy of the charge density and potentials was 240 Ry. The Brillouin zone (BZ) was represented using a $12 \times 12 \times 1$ Monkhorst–Pack grid. To eliminate possible parasitic oscillations of energy during modeling, a vacuum layer of 2.0 nm thickness was added to the considered structure.

The EPW software package [23, 24] was used to model the rates of the electron-phonon interaction. This program was modified to allow the calculation of the imaginary part of the eigenenergy in the case of phonon absorption

$$\text{Im}\left(\sum_{n,\mathbf{k}} e^{-ph}\right) = \pi \sum_{m\nu} \int \frac{d\mathbf{q}'}{\dot{U}_{\text{BZ}}} |g_{mn,\nu}(\mathbf{k}, \mathbf{q})|^2 \times \\ \times (n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}) \delta[(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{F}}) + \omega_{\mathbf{q}\nu} \hbar], \quad (1)$$

and imaginary part of the intrinsic energy in the case of phonon emission

$$\text{Im}\left(\sum_{n,\mathbf{k}} e^{-ph}\right) = \pi \sum_{m\nu} \int \frac{d\mathbf{q}'}{\dot{U}_{\text{BZ}}} |g_{mn,\nu}(\mathbf{k}, \mathbf{q})|^2 \times \\ \times (1 + n_{\mathbf{q}\nu} - f_{m\mathbf{k}+\mathbf{q}}) \delta[(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{F}}) - \omega_{\mathbf{q}\nu} \hbar], \quad (2)$$

where $\hbar$ is the modified Plank constant, $\varepsilon_{m\mathbf{k}+\mathbf{q}}$ is the energy for the branch with number m and point $\mathbf{k}$ in the Brillouin zone (Ω_{BZ}), $\omega_{\mathbf{q}\nu}$ is the phonon frequency with mode ν and wave vector $\mathbf{q}$ in the BZ over which the integration is performed, the parameters $f_{m\mathbf{k}+\mathbf{q}}$ and $n_{\mathbf{q}\nu}$ are the Fermi and Bose distributions, respectively, which are estimated at a given temperature, $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$ is the electron-phonon interaction matrix, $\varepsilon_{\mathbf{F}}$ is the Fermi energy, the symbol δ of the function means the necessity of performing Gaussian smoothing operations during integration.

The rates of the electron-phonon interaction were calculated from the imaginary part of the eigenenergy as [26]

$$\tau^{-1} = \frac{2}{\hbar} \text{Im}\left(\sum_{n,\mathbf{k}} e^{-ph}\right). \quad (3)$$

The following values of the modeling parameters were chosen for modeling in the EPW program of the dependences of electron-phonon interaction rates. So the size of grids of the form $N \times N \times 1$, which corresponded to the

conditional directions of coordinates x, y, z , for electrons during interpolation procedures, was set by the value of the parameter N , the value of which was equal to 300. The values of other modeling parameters were taken as follows: the value of the Gaussian smoothing coefficient (parameter dg) equal to 0.001 eV; the value of the parameter $fsthick$, which determines the value of the range of energies during modeling relative to the Fermi energy level, equal to 2 eV; the number of Wannier functions equal to the value of 12. Parameters $auto_projection$ and $scdm_proj$ sets to value true in modeling. The value of the concentration of electrons was assumed to be $1 \cdot 10^{13} \text{ cm}^{-3}$, and the temperature value was assumed to be 300 K for all presented modeling results.

3. Results of modeling from first principles of electron-phonon scattering rates in graphene and discussion

The dispersive phonon dependences of single-layer graphene are usually considered for modes of the ZA, TA, LA, ZO, TO, LO type [26, 27]. The first group of dependencies, denoted as LA, TA, ZA represents the re-scattering on acoustic phonons along the conventional longitudinal and transverse directions (x, y coordinates), as well as the z coordinate orthogonal to them, respectively. The second group of dependencies, denoted as LO, TO, ZO represents the result of scattering on optical phonons along the conventional longitudinal and transverse directions (x, y coordinates), as well as the z coordinate orthogonal to them, respectively.

The results of modeling the scattering intensities for modes ZA, TA, LA, ZO, TO, LO from energy obtained

in the EPW program using Eqs. (1)–(3) are presented in Figs. 1–12 as blue dots. The obtained point data sets were subjected to approximation using analytic degree functions in the data processing and plotting program ORIGIN (v.8.5) when performing Fitting and Polynomial Fit operations in the Analysis section [28, 29]. When performing these operations in the ORIGIN program, analytical dependencies are obtained with minimal approximation errors. Table 1 presents the results of approximation of the first-principles modeling data for the ZA, TA, LA, ZO, TO, LO modes in the case of phonon absorption for the scattering intensities τ^{-1} having dimension s^{-1} from the energy E having dimension eV. Using the analytical relationships presented in Table 1, curves 1, shown in Figs. 1–6, were plotted.

Curves 2 in Figs. 1–3 and 7–9 represent the scattering rates dependence for the acoustic mode obtained using the formula in [13].

Curves 3 in Figs. 1–3 and 7–9 show the dependence of the scattering rates for the acoustic mode obtained using the formula in [14].

The results of modeling the scattering rates for the acoustic modes ZA, TA, LA from energy in the case of phonon emission, obtained using Eqs. (1)–(3), are presented in Figs. 7–9 as blue-colored dots.

The obtained point data arrays in the case of phonon emission, as well as in the case of phonon absorption, were also subjected to approximation using analytical degree functions in the program for data processing and plotting ORIGIN (v.8.5) when performing Fitting and Polynomial Fit operations in the Analysis section [28, 29].

Table 2 presents the results of the approximation of first-principles modeling data in the case of phonon emission for scattering intensities τ^{-1} , having dimension s^{-1} , from the energy E , having dimension eV.

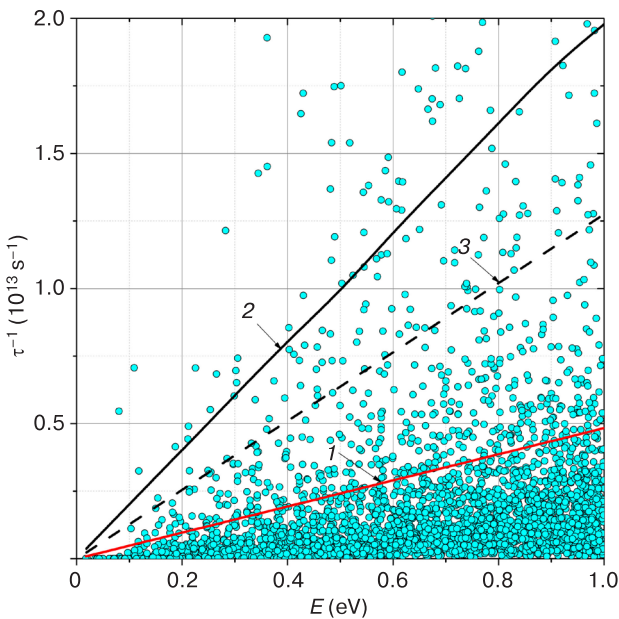


Figure 1. Dependence of the scattering rates for the acoustic mode ZA on energy

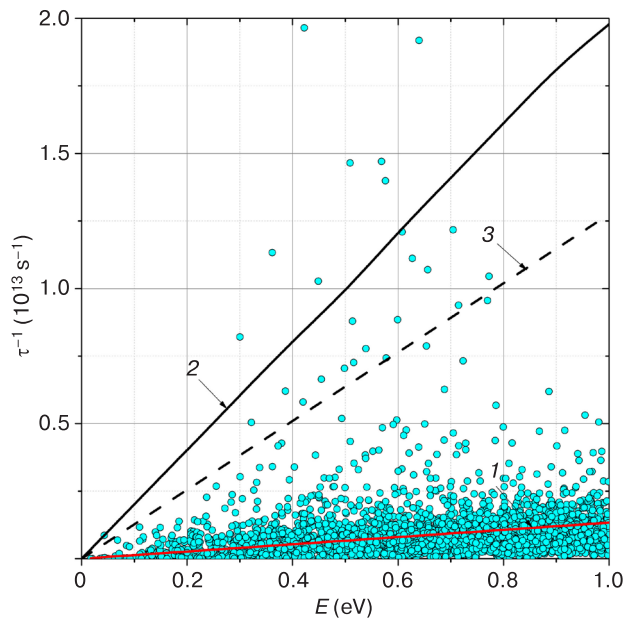


Figure 2. Dependence of the scattering rates for the acoustic mode TA on energy

Table 1. Results of approximation of first-principles modeling data in the case of phonon absorption for the parameter τ^{-1} (s^{-1}) from the energy value E (eV)

Type of mode	Type of dependence	Number of the figure where the dependency is represented as a curve I
ZA	$\tau^{-1} \cdot 10^{13} = 0.483E$	1
TA	$\tau^{-1} \cdot 10^{13} = 0.13065E$	2
LA	$\tau^{-1} \cdot 10^{13} = 0.0948E$	3
ZO	$\tau^{-1} \cdot 10^{13} = 0.0006 + 0.0006E$	4
TO	$\tau^{-1} \cdot 10^{13} = 0.001396 + 0.000941E + 0.00866E^2$	5
LO	$\tau^{-1} \cdot 10^{13} = 0.001519 + 0.00334E$	6

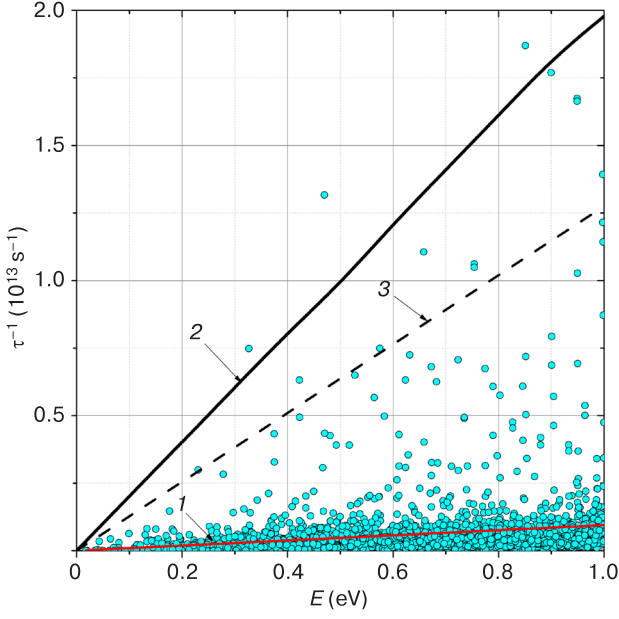


Figure 3. Dependence of the scattering rates for the LA acoustic mode on energy

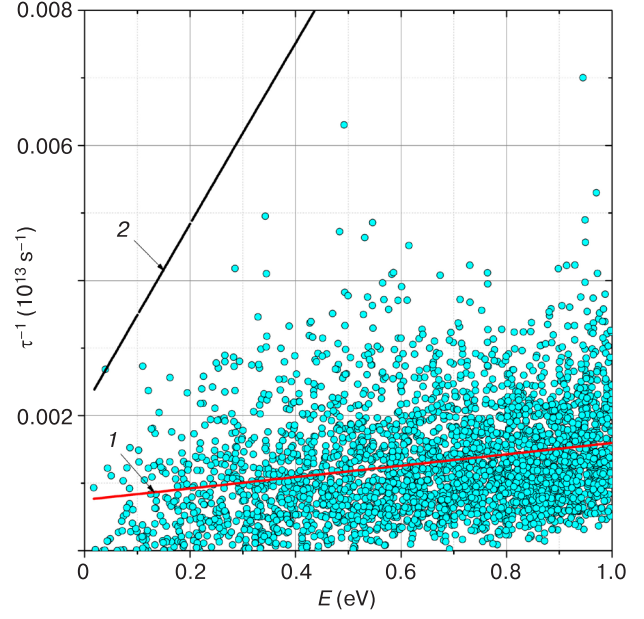


Figure 4. Dependence of the scattering rates for the ZO optical mode on the energy

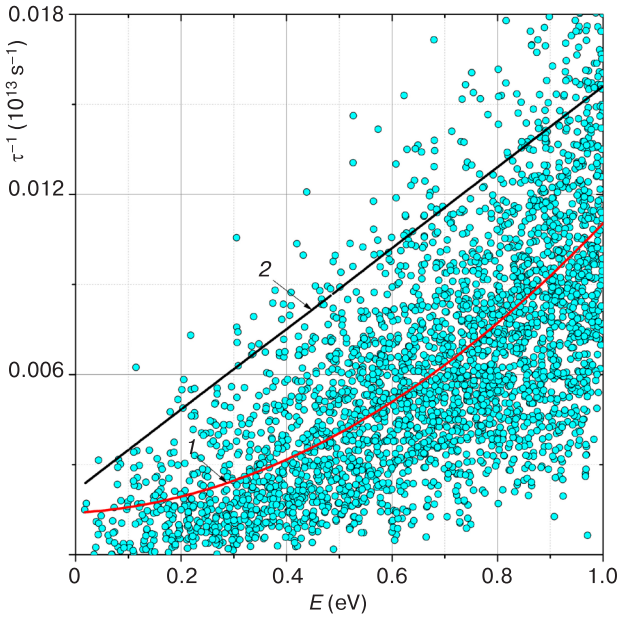


Figure 5. Dependence of the scattering rates for the optical mode of TO on the energy

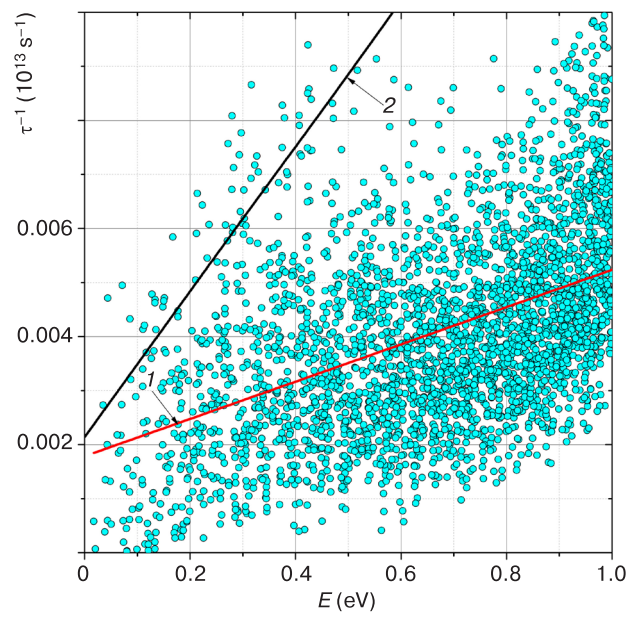


Figure 6. Dependence of the scattering rates for the optical mode LO on the energy

Table 2. Results of approximation of first-principles modeling data in the case of phonon emission for the parameter τ^{-1} (s⁻¹) from the energy value E (eV)

Type of mode	Type of dependence	Number of the figure where the dependency is represented as a curve I
ZA	$\tau^{-1} \cdot 10^{13} = 1.8608E$	7
TA	$\tau^{-1} \cdot 10^{13} = 0.328E$	8
LA	$\tau^{-1} \cdot 10^{13} = 0.08819E + 0.1448E^2$	9
ZO	$\tau^{-1} \cdot 10^{13} = 0.00486 + 0.1343E + 0.5494E^2 - 0.46396E^3$	10
TO	$\tau^{-1} \cdot 10^{13} = 0.402E + 2.3279E^2$	11
LO	$\tau^{-1} \cdot 10^{13} = 0.466E + 4.867E^2 - 2.8306E^3$	12

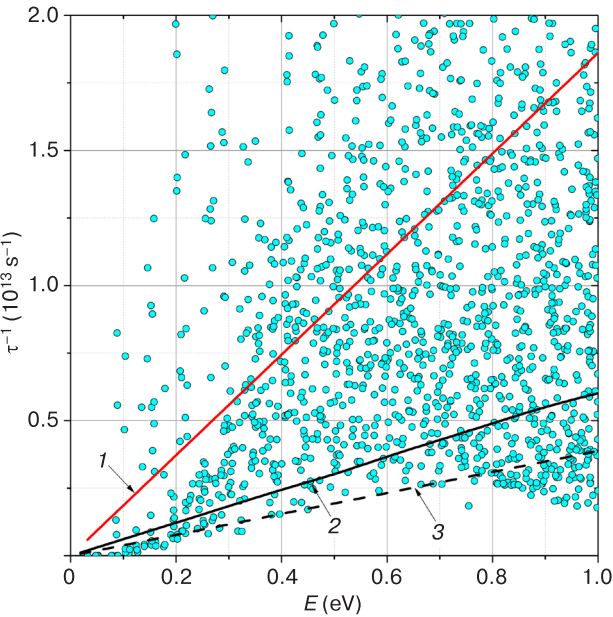


Figure 7. Dependence of the scattering rates for the acoustic mode ZA on the energy

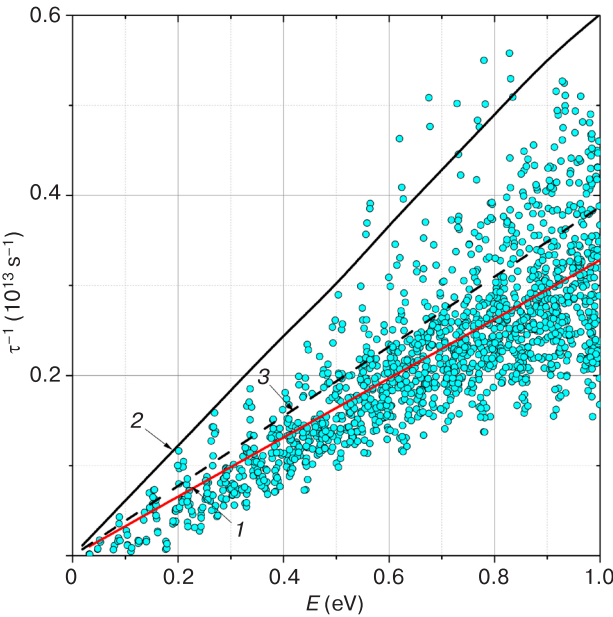


Figure 8. Dependence of the scattering rates for the acoustic mode TA on the energy

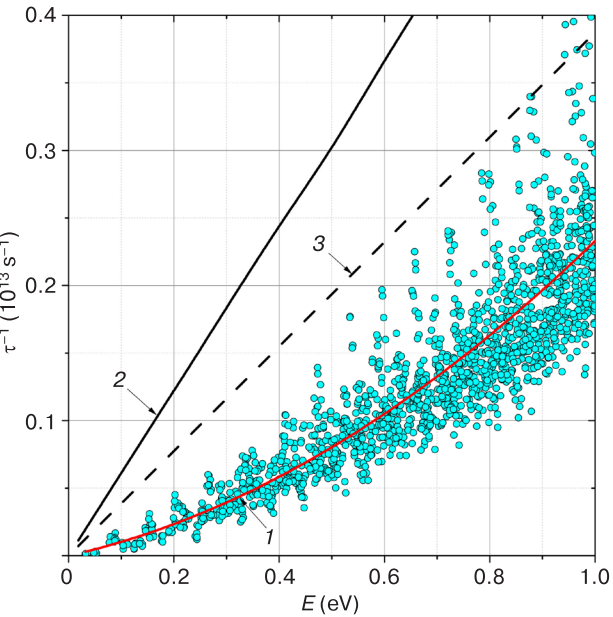


Figure 9. Dependence of the scattering rates for the LA acoustic mode on energy

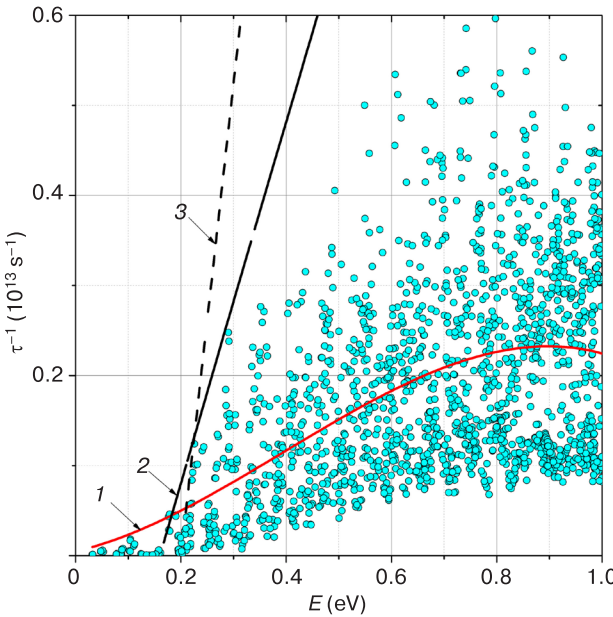


Figure 10. Dependence of the scattering rates for the ZO optical mode on the energy

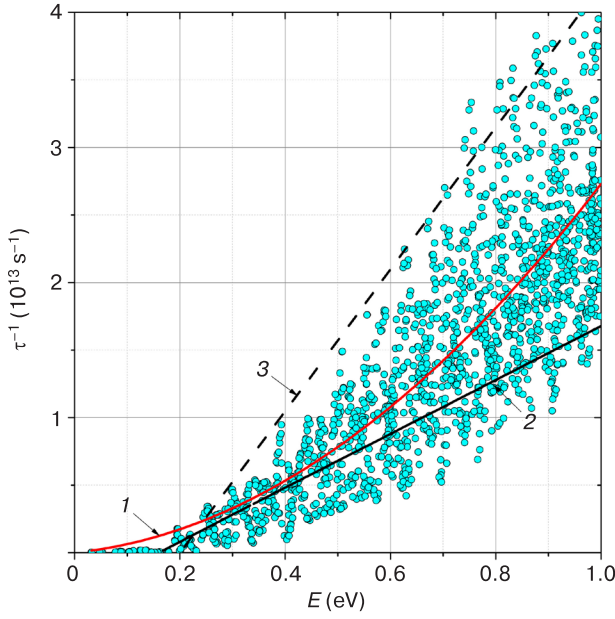


Figure 11. Dependence of the scattering rates for the optical mode of TO on the energy

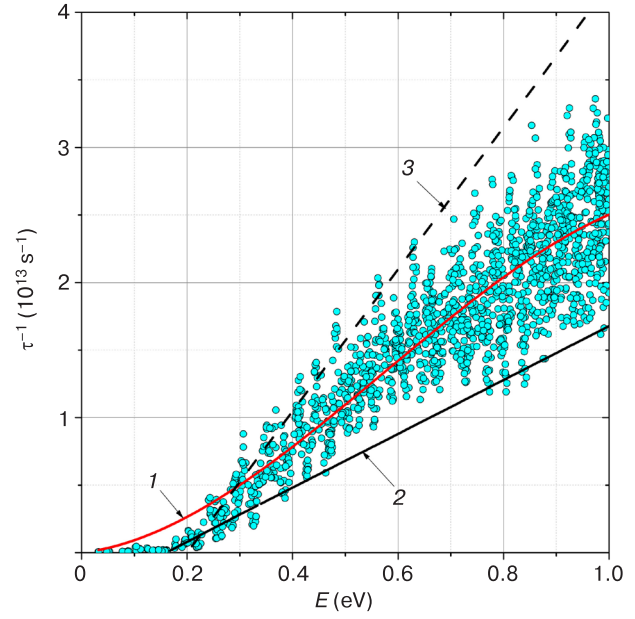


Figure 12. Energy dependence of the scattering rates for the LO optical mode

Using the analytical relationships presented in Table 2, the curves 1 presented in Figs. 7–12.

Curve 2 in Figs. 4–6 and 10–12 shows the dependence of the scattering rates for the optical mode obtained using the formula in [13]. Curve 3 in Figs. 10–12 represents the dependence of the scattering rates for the optical mode obtained using the formula in [14].

Using the data presented in Tables 1 and 2, we can perform a comparative analysis of the energy dependences of the scattering rates in the cases of phonon absorption and emission. Fig. 13 shows the energy dependences of the scattering rates in the case of phonon emission (a) and in the case of phonon absorption (b) obtained using the formulas presented in Tables 2 and 1, respectively.

Curves 1–3 in Fig. 13a represent the energy dependences of the scattering rates for the acoustic mode ZA, optical modes LO and TO, respectively. Curves 4–6 in Fig. 13a represent the energy dependences of the scattering rates for acoustic mode TA, optical mode ZO, and acoustic mode LA, respectively.

Curves 1–3 in Fig. 13b shows the energy dependences of scattering rates for acoustic modes ZA, TA, LA, respectively. Curves 4–6 in Fig. 13b represents the energy dependences of scattering rates for optical modes ZO, TO, LO, respectively.

The analysis of Fig. 13a shows that the largest scattering rates in the case of phonon emission in the considered energy range up to 1 eV are observed for the

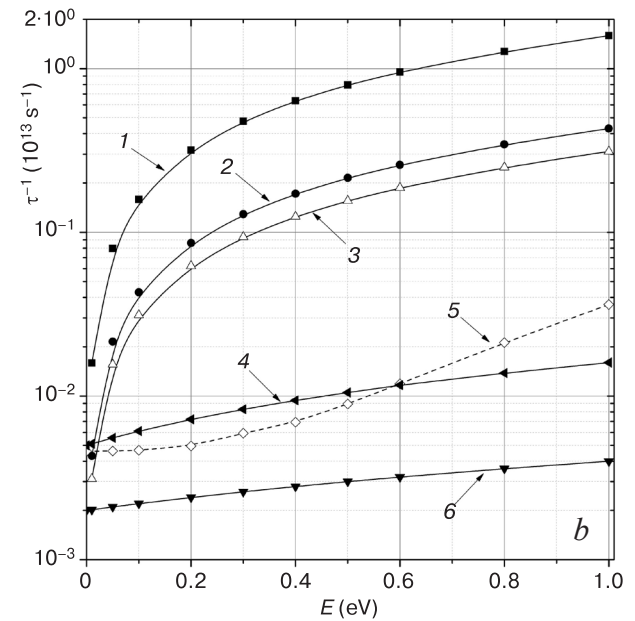
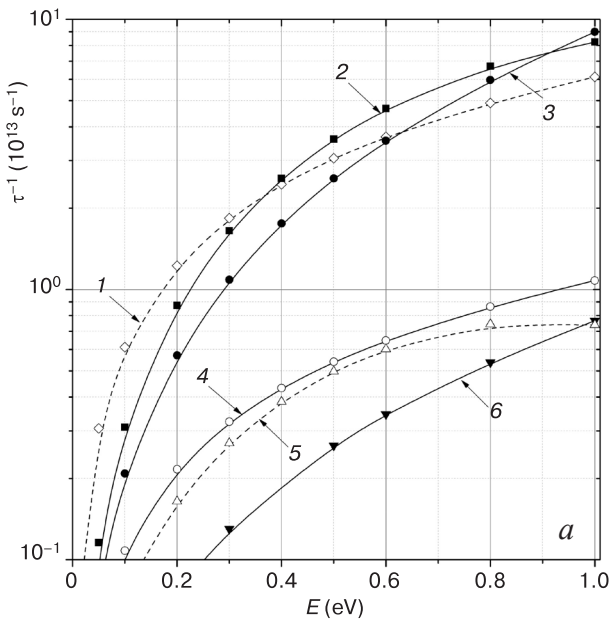


Figure 13. Energy dependences of scattering rates in the case of phonon emission (a) and in the case of phonon absorption (b)

optical modes LO and TO, as well as for the acoustic mode ZA.

The scattering rates for the other modes, TA, LA, and ZO, are significantly, approximately by an order of magnitude, smaller than the scattering intensities for the LO, TO, and ZA modes.

From the presented data, we can see that the difference in the scattering rates for the above two groups of modes (LO, TO, and ZA) and (TA, LA, and ZO) is not as significant as the difference between the modes (TA, LA, LO, TO) and the modes (ZA and ZO) obtained in [19] for the energy range 0.2–0.4 eV, and is approximately 5–7 orders of magnitude.

It is noteworthy that the scattering rates of the ZA mode is comparable to that of the LO and TO modes.

The analysis of Fig. 13b shows that the largest scattering rates in the case of phonon absorption in the considered energy range up to 1 eV are observed for the acoustic modes ZA, TA, LA, with the scattering rates for the acoustic mode ZA prevailing over other scattering intensities. The scattering intensities for the other modes – ZO, TO, LO – are significantly, approximately by an order of magnitude or two, less than the scattering rates for the ZA, TA, LA modes. It can be seen from the presented data that the difference between these two groups

of modes is much smaller than the difference obtained in the case of phonon absorption in [19] between the modes (TA, LA, LO, TO) and the modes (ZA and ZO) in the energy range of 0.2–0.4 eV. In general, at the same energy values, the magnitude of the scattering rates in the case of phonon emission dominate over the magnitude of the scattering rates in the case of phonon absorption, which can be seen from the comparison of the data presented in Figs. 13 (a and b).

4. Conclusion

The results of the study of electron scattering rates on acoustic and optical phonons in a single layer of graphene without a substrate at non-large energy values, which do not exceed the value of 1 eV, are presented. In the first-principles modeling for modes of the ZA, TA, LA, ZO, TO, LO type, which are observed in graphene, the electron scattering rates for the cases of phonon emission and phonon absorption are obtained. The presented dependences and parameters of electron scattering rates on acoustic and optical phonons in graphene can serve as a basis for modeling of new heterostructure devices containing graphene and other semiconductor materials.

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