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Spatio-temporal dynamics in graphene

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Temporally and spectrally resolved dynamics of optically excited carriers in graphene has been intensively studied theoretically and experimentally, whereas carrier diffusion in space has attracted much less attention. Understanding the spatio-temporal carrier dynamics is of key importance for optoelectronic applications, where carrier transport phenomena play an important role. In this work, we provide a microscopic access to the time-, momentum-, and space-resolved dynamics of carriers in graphene. We determine the diffusion coefficient to be $D \approx 360 \text{ cm}^2 \text{s}^{-1}$ and reveal the impact of carrier–phonon and carrier–carrier scattering on the diffusion process. In particular, we show that phonon-induced scattering across the Dirac cone gives rise to back-diffusion counteracting the spatial broadening of the carrier distribution.

The time- and momentum-resolved carrier dynamics in graphene is meanwhile well understood, but there have been only a few studies on spatio-temporal dynamics and diffusion in graphene and other low dimensional materials, such as carbon nanotubes and transition metal dichalcogenides.

Kulig et al. studied the exciton diffusion in WS$_2$ and determined that the diffusion coefficient varies over two orders of magnitude with respect to the pump fluence. In graphene, pump–probe experiments performed at relatively high pump fluences demonstrated a diffusion coefficient of $D = 250 \pm 140 \text{ cm}^2 \text{s}^{-1}$ on a picosecond timescale after optical excitation. The diffusion of photoexcited carriers has been studied theoretically with an effective Boltzmann approach, where many-particle scattering has been only considered with relaxation rates.

However, a full microscopic view on the spatio-temporal dynamics revealing the interplay between diffusion and momentum- and time-dependent scattering processes is still missing.

Exploiting the density matrix formalism and the Wigner representation, we provide microscopic insights into the temporally, spectrally, and spatially resolved dynamics of optically excited carriers in graphene including carrier diffusion, carrier–light, carrier–phonon, and carrier–carrier scattering processes on the same microscopic footing, cf. Fig. 1. In particular, we determine the diffusion coefficient and show that the diffusion process can be tuned with experimentally accessible knobs, such as pump fluence, substrate and temperature. Furthermore, we reveal how carrier–phonon scattering counteracts the diffusion through efficient scattering across the Dirac cone resulting in an efficient back-diffusion, cf. Fig. 1(b).

Theoretical approach

We consider a graphene sheet under local optical excitation (red arrows in Fig. 1). The optically excited carriers relax to lower energies via Coulomb- (orange arrows) and phonon-
induced scattering (green arrows). The inhomogeneous optical excitation creates spatial gradients in the carrier density, giving rise to diffusion of carriers (purple arrows). To obtain microscopic access to the spatio-temporal dynamics, we derive a set of coupled equations of motion for the electron occupation probability \( \rho^e_k(t) \), the microscopic polarization \( p_k(t) \), and the phonon number \( n^\lambda_j(t) \). Here, we consider fluctuations of the occupation probability \( \rho^e_k(t) = \langle a_k^\dagger(t) a_k(t) \rangle \), the microscopic polarization \( p_k(t) = \langle a_k(t) a_k(t) \rangle \), and the hole occupation probability is \( \rho^h_k(t) = 1 - \rho^e_k(t) \). The corresponding phonon operators are \( b^j_q(t), b^j_q(t) \) with the phonon mode \( j \) and the phonon momentum \( q \).

To introduce spatial effects, we transform the occupation probability into the Wigner formalism.\(^{22,23} \) Here, we perform a Fourier transformation resulting in the momentum representation probability \( \rho^e_k(q) \), the microscopic polarization \( p_k(q) \), and the phonon number \( n^\lambda_j(q) \). Details on the contri-

Finally, the equation of motion for the Wigner function for the free Hamilton operator reads

\[
\mathcal{J}_k^f(t) = -\frac{1}{\hbar} \left[ \mathbf{V}_k \mathbf{f}_k^f(t) - \mathbf{V}_r \mathbf{f}_k^r(t) \right].
\] (2)

To derive the equations of motion for the Wigner function, the polarization and the phonon number with the full Hamilton operator we make the following assumptions: (i) We consider diffusion processes in the polarization to be small, since the latter quickly decays in momentum space and vanishes directly after the optical excitation.\(^5 \) In contrast, the relaxation of carriers occurs on a picosecond timescale which is comparable to diffusion processes, and therefore the diffusion term can not be neglected in the equation for the Wigner function. (ii) We also neglect the phonon diffusion, since it is expected to be much slower than the electronic diffusion due to the flat phonon dispersion. (iii) We expect scattering processes between different spatial positions to be small compared to the diffusion. Now, using the Heisenberg equation of motion, we derive the full spatio-temporal graphene Bloch equations in second-order Born-Markov approximation

\[
\mathcal{J}_k^f(t) = \Gamma_{ki}^c(\mathbf{f}_k^f(t) - \mathbf{f}_i^c(t)) - \mathbf{V}_k^c \mathbf{f}_k^f(t) + 2 \text{Im} \{ \Omega_{ki}^c(\mathbf{f}_k^f(t) - \mathbf{f}_i^c(t)) \} + \mathbf{V}_k^c \mathbf{f}_k^f(t),
\]

\[
\rho_{ki}^c(t) = i\Delta\omega_k(\mathbf{r}, t) \mathbf{p}_k(t) - i\frac{\hbar}{2} \mathbf{V}_k^{ci} \mathbf{f}_k^f(t),
\]

\[
\mathcal{N}_{ki}^c(t) = \Delta\omega_k(\mathbf{r}, t) \mathbf{p}_k(t) - 1, \mathcal{N}_{ki}^h(t) = 1 + \mathcal{N}_{ki}^c(t) - \mathcal{N}_{ki}^h(t),
\]

\[
\mathcal{N}_{ki}^h(t) = 1 - \mathcal{N}_{ki}^c(t) - \mathcal{N}_{ki}^h(t),
\]

The equations describe the time-, momentum- and space-resolved coupled dynamics of electrons/holes, phonons, and the microscopic polarization. The dynamics of electrons in the conduction band and holes in the valence band is symmetric, but has different initial conditions for doped graphene samples. The appearing Rabi frequency is defined as

\[
\Omega_{ki}^c(\mathbf{r}, t) = \frac{e_0 \mathbf{M}^{ei}_{ki} \cdot \mathbf{A}(\mathbf{r}, t)}{m_0},
\]

with the vector potential \( \mathbf{A}(\mathbf{r}, t) \), and the optical matrix element \( \mathbf{M}^{ei}_{ki} = \langle \mathbf{v}_k | \mathbf{V}_k | \mathbf{k}_c \rangle \). Since we study the carrier dynamics close to the Dirac point, renormalization effects can be neglected. Furthermore, we have introduced \( \hbar \Delta\omega_k(\mathbf{r}, t) = (\epsilon_{ki}^c - \epsilon_{ki}^h + i\gamma_h(\mathbf{r}, t)) \) with the electronic dispersion \( \epsilon_{ki}^c \) and the dephasing rate \( \gamma_h(\mathbf{r}, t) \). The time-, momentum- and spatial dependent dephasing \( \gamma_h(\mathbf{r}, t) \) and in- and out-scattering rates \( \Gamma_{ki}^{\text{in/out}}(\mathbf{r}, t) \) include carrier–carrier and carrier–phonon scattering channels. The dynamics of the phonon number \( n^\lambda_j(t) \) is driven by the emission and absorption rates \( \Gamma_{ki}^{\text{em/abs}}(\mathbf{r}, t) \). The constant \( \gamma_{ph} \) is the experimentally determined phonon decay rate.\(^{24} \) More details on the appearing many-particle scattering and dephasing rates can be found in ref. 1 and 5. In this work,
we assume that graphene lies on a SiC-substrate and is surrounded by air on the other side. This is taken into account by introducing an averaged dielectric background constant
\[ \epsilon_{bg} = \frac{1}{2}(\epsilon_s + 1), \]
where \( \epsilon_s = 9.66 \) is the static screening constant of the substrate, while 1 describes the dielectric constant of air. Furthermore, the internal many-particle screening is taken into account by calculating the static limit of the Lindhard equation,\(^{10,26}\) which screens the Coulomb matrix elements.

The derived set of equations resemble the semiconductor Bloch equations for spatial homogeneous systems (cf. ref. 1 and 5) up to the additional term
\[ V_{kk'} = q \cdot V_{k} \cdot f_{k}(r, t), \]
which describes the diffusion of carriers in the direction \( V_{kk'} \propto \epsilon_k = k/|k| \). As a result, carriers with different sign in momentum move in opposite directions generating locally asymmetric carrier distributions in momentum space and resulting in a local current
\[ j(r, t) = -\frac{4e \epsilon_0 \rho_p}{A} \sum_k f_k(r, t) \epsilon_k \text{ with the Fermi velocity } v_F. \]
The sum contains both electrons in the conduction band and holes in the valence band and in a spatially homogeneous system, the mean current vanishes.

### Spatio-temporal dynamics

Now, we numerically evaluate the spatio-temporal graphene Bloch equations and investigate the interplay of diffusion and relaxation processes after optical excitation. We excite carriers with an optical pulse with a Gaussian profile both in time and space. We chose typical values for pulse characteristics including a temporal FWHM of 115 fs, a spatial FWHM of 265 nm, an excitation energy of 1 eV and a pump fluence of 1 \( \mu J \) cm\(^{-2}\).

The temporally and spatially dependent carrier density \( n(x, t) \) is shown in Fig. 2(a). The diffusion of carriers is reflected in the broadening of the carrier density in space. Normalizing the density for each time step, the broadening becomes more visible (Fig. 2(b)), since phonon- and Auger-driven interband processes give rise to a reduction of carriers with increasing time. Fig. 2(c) shows the temporal and spatial distribution of the electronic temperature. The latter has been determined via the average kinetic energy per particle. Assuming a Fermi distribution, one obtains
\[ \sum_k \epsilon_k \rho_k / \sum_k \rho_k \approx 2.2k_B T. \]

That shortly after the pulse the carrier distribution deviates from an equilibrium Fermi distribution and therefore the temperature is there not well defined.

To quantify the diffusion and to estimate the diffusion coefficient for graphene, we fit the carrier density with a Gaussian \exp(-x^2/w^2(t)) for every time step. The temporal evolution of the width \( w(t) \) is depicted in Fig. 2(d). It is connected to an effective diffusion coefficient \( D \) via\(^{27}\) \[ w(t) = w_0 \sqrt{4Dt} \]
resulting in \( D \approx 360 \text{ cm}^2 \text{ s}^{-1} \) for the investigated graphene sample on a SiC substrate. Our results fit well to the experimentally obtained values\(^{17}\) for the diffusion coefficient of \( D = 250 \pm 140 \text{ cm}^2 \text{ s}^{-1} \). In Fig. 2(e) we show the influence of pump fluence, substrate and temperature on the diffusion coefficient.

We find that the temperature has the largest impact. The underlying processes will be discussed later.

So far we have investigated the diffusion behaviour by taking into account the full carrier dynamics. Now, to understand the fundamental interplay of many-particle scattering and diffusion processes we study separately the impact of different scattering mechanisms on the diffusion process, cf. Fig. 3. We start with the case without any scattering channels just considering the electron–light interaction. After the optical excitation, carriers with positive/negative momenta diffuse in opposite spatial directions according to the diffusion term in eqn (3). After approximately 100 fs the carrier separation becomes visible, as the initial carrier density distribution splits into two pronounced peaks of the same width but with half of the amplitude, cf. Fig. 3(a). Including the carrier–phonon scattering, we observe a strongly reduced spatial broadening of the carrier density and no splitting appears (Fig. 3(a)). Phonon-induced relaxation processes counteract the diffusion \( \text{via back-scattering across the Dirac cone and the following back-diffusion (cf. Fig. 1).} \]
The impact of carrier–phonon scattering will be further microscopically resolved in the next section. Including only the carrier–carrier scattering, the density diffuses with the same speed as in the case without any scattering channels (cf. Fig. 3(c)). This is a consequence of the symmetry of Coulomb matrix elements, which favor parallel scattering.\(^{28,29}\) Scattering across the Dirac
Section carriers with positive/negative momentum diffuse in opposite spatial direction. This behaviour is illustrated in Fig. 4(c), where carriers with positive momentum diffuse from $x < 0$ positions (orange spots) to $x > 0$ positions (red spots). After 1 ps the carriers have already relaxed to energies close to the Dirac cone and below the optical phonon energy. Consequently, the scattering with acoustic phonons becomes dominant. Due to the flat dispersion of acoustic phonons with respect to the Dirac cones back-scattering across the Dirac cone is preferred, such that carriers with positive momenta are scattered to negative momenta and vice versa (Fig. 1). The inversion of momenta results in a back-diffusion, such that the overall carrier distribution stays bunched in space, cf. Fig. 3(b). The back-diffusion is shown in Fig. 4(d) by the multiple sign change in the colored regions (red to orange to red).

**Carrier–carrier dynamics**

Now, we investigate the impact of carrier–carrier scattering on diffusion of optically excited carriers. An important aspect here is that Auger scattering is efficient giving rise to a carrier multiplication that increases the overall carrier density (note the scale of the color map in Fig. 5 compared to Fig. 4(a)). This also results in a quick increase of the carrier distribution close to the Dirac cone already during the optical excitation (Fig. 5(a)). Since electrons and holes diffuse in the same direction, the conditions for carrier multiplication are still satisfied after the diffusion. The directional dependence (in momentum space) for intraband carrier–carrier scattering...
diusion and back-diusion of diusion formalism in Wigner representation. We investigate the temporal carrier dynamics in graphene based on the density after a local optical excitation. In particular, we determine a diffusion coefficient of \( D \approx 360 \text{ cm}^2 \text{s}^{-1} \) that agrees well with recent experimental values. Furthermore, we reveal that carrier–phonon scattering across the Dirac cone and the resulting back-diusion are crucial ingredients to understand the spatial broadening of the carrier distribution. The gained insights are important e.g. for graphene-based photodetectors,\(^{15–19}\) that are governed by the thermoelectric effect, which relies on spatial temperature gradients.

**Conflicts of interest**

There are no conflicts to declare.

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**References**