Transient charge and energy balance in graphene induced by ultrafast photoexcitation

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Abstract

Ultrafast optical pump–probe spectroscopy measurements on monolayer graphene reveal significant optical nonlinearities. We show that strongly photoexcited graphene monolayers with 35 fs pulses quasi-instantaneously build up a broadband, inverted Dirac-fermion population. Optical gain emerges and directly manifests itself via a negative conductivity at the near-infrared region for the first 200 fs, where stimulated emission completely compensates for absorption loss in the graphene layer. To quantitatively investigate this transient, extremely dense photoexcited Dirac-fermion state, we construct a two-chemical-potential model, in addition to a time-dependent transient carrier temperature above the lattice temperature, to describe the population inverted electronic state metastable on the time scale of tens of femtoseconds generated by a strong exciting pulse. The calculated transient optical conductivity reveals a complete bleaching of absorption, which sets the saturation density during the pulse propagation. In particular, the model calculation reproduces the negative optical conductivity at lower frequencies in the states close to saturation, corroborating the observed femtosecond stimulated emission and optical gain in the wide near-infrared window.

(Some figures may appear in colour only in the online journal)

1. Introduction

Despite the well-established linear optical properties in graphene, which is marked by a universal absorption $A = \pi \alpha = 2.3\%$ ranging from near-infrared to visible light [1–3], significantly less attention has been paid to the ultrafast nonlinear optical properties. Important for future photonic and optoelectronic applications [4], carrier dynamics in graphene after being driven far out of equilibrium needs to be understood. However, ultrafast spectroscopy studies have been reported recently showing unusual properties [5–21]. In particular, the observation of nonlinear absorption when applying an ultrashort intense laser pulse to monolayer graphene reveals an extremely dense, quasithermal photoexcited carrier state created by strong pumping on a 10 fs time scale and metastable for several tens of femtoseconds, which implies a unique transient electronic state in the important emerging material graphene [18].

When strongly driven out of equilibrium by coherent light, the excited carriers subsequently participate in several dynamical processes while relaxing back to equilibrium. Among them are carrier decoherence, thermalization, cooling, and electron–hole recombination. If the excitation pulse is short enough, by observing the responses following from right after the pump, we can identify the typical time scales associated with these processes. Facilitated by recent ultrafast spectroscopy measurements, some progress has been made. It is recognized that the ultrafast carrier dynamics in graphene...
Figure 1. Schematic illustration of the formation of a population inverted electronic state in the intermediate time $t_{eh} < t < t_{c,r}$: (a) Photoexcited carriers generated by the $\sim 10$ fs pump pulse; (b) the leading scattering processes of photoexcited carriers taking place in several femtoseconds: $e + e \rightarrow e + . e$, $h + h \rightarrow h + h$, $e + h \rightarrow e + h$, which quickly establish individual thermalization in electron- and hole-carriers sharing a common electronic temperature $T_e$ due to the electron–hole scattering events. (c) After the internal thermalization, the photoexcited carriers form a population inverted hourglass-like electronic state characterized by two chemical potentials and a common electron temperature.

This paper focuses on this unique transient electronic state and provides details on ultrafast optical pump–probe spectroscopy measurements on monolayer graphene to reveal significant ultrafast optical nonlinearities, including nonlinear absorption saturation and near-infrared stimulated emission. These properties arise from a broadband, inverted Dirac-fermion population induced by 35 fs pulse excitation. Optical gain emerges and directly manifests itself via a negative conductivity at the near-infrared region for the first hundreds of femtoseconds, where stimulated emission completely compensates absorption loss in the graphene layer. To quantitatively investigate this transient, extremely dense photoexcited Dirac-fermion state, we construct a simple model of a quasithermalized distribution with one electron temperature but two distinct chemical potentials associated with the electron- and hole-band, respectively. We find this transient state associated with a high electron temperature $T_e$ up to 3000–4000 K, which causes a broadband distribution extending to high energy that naturally explains the observed blue-shifted component in the photoluminescence spectrum. We further explore the phase space capacity, identify the maximal photoexcitation density restricted by phase space filling, and the individual chemical potential of each band is calculated. To understand the observed nonlinear optical behavior and the measured large saturation density, we calculate the optical conductivity for this nonequilibrium electronic state. The results show that the available phase space cannot be completely filled but will be saturated at a lower photoexcitation density due to the balance between absorption and emission. This calculated saturation density is in excellent agreement with the experimental value. Most interestingly, our model reproduces the experimental results that the nearly-saturated states created by a high-frequency pump are unstable to a low-frequency pulse through stimulated emission to bring the system to a lower-level metastable state (illustrated in figure 2), resulting in an optical gain phenomenon within the first hundreds of femtoseconds after photoexcitation. The excellent agreement between theory and experiment further corroborates that our simple model captures the feature of the transient state on an early time scale ($<100$ fs) in the high excitation regime. Meanwhile, the comparison with the measured optical conductivity disfavors the equal-chemical-potential model as describing the transient states in graphene at the femtosecond time scale—an outstanding issue debated in the community.
2. Experimental details

2.1. Spectroscopy measurement

The experimental setup is shown in figure 3. In our experiment, a Ti:Sapphire amplifier with center wavelength 800 nm, pulse width 35 fs at 1 kHz repetition rate is used. This further drives optical parametric amplifiers tunable with tunable optical pump pulses covering 572–2400 nm, allowing both degenerate and non-degenerate pump/probe spectroscopy. The laser is further split into pump and probe paths. The pump beam, chopped at a half harmonic of the laser repetition rate, directly excites the sample. The reflection of the probe beam, together with the reference, is fed into an auto-balance detector, and the individual beams as well as the difference between them are picked up by three boxcar integrators. During the measurement, the pump fluence from a few $\mu$J cm$^{-2}$ to the mJ cm$^{-2}$ level is finely controlled. This way we can record pump-induced differential reflectivity changes $R/R$ with $\sim 40$ fs time resolution and signal-to-noise ratios down to $5 \times 10^{-5}$. Similar experimental setups and details are described elsewhere, e.g., see [27–32].

2.2. Samples

Graphene was prepared from the thermal evaporation of SiC [33] with the substrates used in the current experiments 6H-SiC(0001) purchased from Cree, Inc. The samples were graphitized in UHV ($P \sim 1 \times 10^{-10}$ Torr) by direct current heating of the sample to $\sim 1300^\circ$C, as measured with an infrared pyrometer, with the reading of the pyrometer adjusted to take account of the emissivity of graphite reported in the literature [34]. The sample was not pretreated in an H$_2$ atmosphere within a furnace, which is a common practice because it excludes the formation of multi-step heights and allows easier control of the thickness. The layer thickness (whether single layer G1 or bilayer G2) was controlled by the heating rate: faster one-step heating rates (within 2–3 s to reach $1300^\circ$C) result in large G1 domains while multiple heating steps with a slower rate (30 s to reach $1350^\circ$C) result in samples with large G2 areas. The graphene thickness was identified using contrast thickness [35], giving step height changes between different regions which were found to be combinations of only two steps, i.e., 0.25 nm (of SiC) and 0.33 nm (of graphene), as explained in [33]. Figure 1(c) in [18] shows a large 2 $\mu$m $\times$ 2 $\mu$m (left) G1 area formed after heating at the fast rate. The atomic scale image is shown to the right, where the 1 $\times$ 1 unit cell is seen with a lattice constant 0.246 nm and intensity modulation due to the $6\sqrt{3}$ is also seen. The tunneling conditions are $-0.5$ V, 1 nA. The high intensity of the modulation and the resolution of the six atoms of the graphene ring indicate that this is predominantly G1 (in excess of 90% of the area). The detailed growth conditions, characterizations and doping ($\sim 0.4$ eV for monolayer) of the obtained epitaxial graphene on SiC are extensively established by our papers [33, 36] and many others in the literature, e.g., [37–39].

3. Threshold reflection coefficient and optical gain

Considering graphene on a substrate with dielectric constant $\varepsilon_s$, the amplitude of the reflected and transmitted waves for a normally incident beam follow from Maxwell’s equations along with the usual boundary conditions:

$$
\hat{r} = \frac{1 - n_s - 4\pi\sigma(\omega)/c}{1 + n_s + 4\pi\sigma(\omega)/c},
\hat{t} = \frac{2}{1 + n_s + 4\pi\sigma(\omega)/c}.
$$

Here $\sigma(\omega)$ is the complex optical conductivity. The common reflection and transmission coefficients are determined by $R = |\hat{r}|^2$ and $T = n_t |\hat{t}|^2$. If $\sigma = 0$ then $R + T = 1$. The presence of a finite conductivity in the graphene sheet leads to an absorption

$$
A_g = \frac{1}{2} (1 + n_s)^2 (1 - T - R).
$$
where it is customary [2] to introduce the coefficient \((1 + n_s)^2/4\) such that \(A_g\) corresponds to the absorption coefficient of a suspended graphene sheet.

Following [2] we can introduce the reflection of the substrate (for \(\sigma = 0\))

\[
R_s = \left( \frac{1 - n_s}{1 + n_s} \right)^2
\]

(3)

and of the substrate with graphene \(R_{s+g}\)

\[
R_{s+g} = \left| \frac{1 - n_s - 4\pi \sigma(\omega)/c}{1 + n_s + 4\pi \sigma(\omega)/c} \right|^2.
\]

(4)

For the complex optical conductivity of graphene in equilibrium and at \(T = 0\) it holds that

\[
\sigma_{eq}(\omega, T = 0) = \frac{e^2}{4\hbar} \left( \theta(\omega - 2\mu) - \frac{i}{2\pi} \ln \left( \frac{\omega + 2\mu}{\omega - 2\mu} \right) \right).
\]

(5)

Near the jump in the optical conductivity at \(\omega = 2\mu\), the imaginary part of the conductivity has a logarithmic divergence, which is smeared out in case of finite temperatures. Since \(\sigma(\omega)\) is of the order of \(e^2/\hbar\), it holds that \(\sigma(\omega)/c\) is of the order of the fine-structure constant of quantum electrodynamics \(\alpha_{QED} = e^2/(\hbar c) \approx 1/137 \ll 1\). This allows an expansion in \(\sigma(\omega)/c\). It follows that

\[
\frac{R_{s+g} - R_s}{R_s} = \frac{4 \pi}{n_s - 1} \sigma'(\omega) + O(\alpha_{QED}^2)\]

(6)

Thus, the reflection coefficient to leading order in \(\alpha_{QED}\) is fully determined by the real part of the optical conductivity \(\sigma'(\omega) = \text{Re} \sigma(\omega)\), the imaginary part only entering at higher orders. For the transmission and absorption coefficients it follows in the same limit that

\[
T = \frac{4n_s}{(1 + n_s)^2} - \frac{8n_s}{(n_s + 1)^3} \frac{4\pi}{c} \sigma'(\omega) + O(\alpha_{QED}^2)
\]

\[
A_g = \frac{4\pi}{c} \sigma'(\omega) + O(\alpha_{QED}^2).
\]

(7)

This yields the result

\[
\frac{R_{s+g} - R_s}{R_s} = \frac{4 \pi}{n_s - 1} A_g\]

(8)

of [2].

Equation (6) enables us to determine a threshold value for the reflectivity that corresponds to a negative optical conductivity and thus to a behavior with optical gain. From equation (6) it follows for the reflection after delay time \(\tau\) that:

\[
\Delta R/R = \frac{R_{s+g}(\tau) - R_{s+g}(0)}{R_s} = \frac{4 \pi}{n_s - 1} \frac{A_g(\tau) - A_g(0)}{R_{s+g}(0)}\]

(9)

Using the experimentally established value \(\sigma'(0) = e^2/(4\hbar)\) for the optical conductivity prior to the pulse, it follows that

\[
\sigma'(\tau) < 0 \text{ if } \Delta R/R < \Delta R/R_c, \text{ where } \Delta R/R_c = -\frac{4\pi \alpha_{QED}}{n_s^2 - 1}.\]

(10)

With \(n_s = 2.7\) it follows that \(\Delta R/R_c = -1.4582\%\). If for some reason the dielectric constant of the substrate is larger than 2.7, this would only reduce the critical value of \(\Delta R/R\) and we would only underestimate the regime where \(\sigma < 0\). Given that our data yield the magnitude of \(\Delta R/R\) as large as 1.9\%, it follows that we have \(\sigma < 0\) as long as \(n_s > 2.41\). In the literature, the uncertainty of \(n_s = 2.7\) is \(\pm 0.1\). The smallest index of SiC is 2.55 in the THz range. These results demonstrate that our conclusion \(\sigma < 0\) is robust.

More convincingly, in figure 4, we experimentally determine the existence and value of the threshold \(\Delta R/R_c = -1.4582\%\) for zero conductivity in our sample. This further demonstrates unambiguously that the reflectivity geometry in the present sample provides a direct measurement of the real part of conductivity \(\sigma\) of the graphene layer (or absorption), which directly accesses the gain/loss processes. This also demonstrates again that our sample is a graphene monolayer, consistent with the conclusion from STM.

Using the same reasoning we can relate the reflectivity to the absorption coefficient

\[
R_{s+g}(\tau) = \frac{n_s - 1}{n_s + 1} \frac{4}{(1 + n_s)^2} A(\tau)\]

(11)

and obtain

\[
\frac{A_g(\tau) - A_g(0)}{A_g(0)} = \frac{R_{s+g}(\tau) - R_{s+g}(0)}{R_{s+g}(0)} \frac{1}{1 + 4A_g(0)}\]

(12)

which will be used in our analysis of the density of transient electrons and holes, where \(A_g(\tau = 0) = \pi \alpha_{QED}\).

4. Stimulated infrared emission and optical gain

Here we provide a set of pump fluence dependence data at a probe photon energy of 1.33 eV, as shown in figures 5(a) and (b). Our conclusions with respect to stimulated emission and...
optical gain are based on the observed negative conductivity in strongly photoexcited graphene, which is fully consistent with the complementary data presented in [18]. In addition, following a similar analysis equations (6) and (7), the differential transmission of our sample can be extracted from information on the differential reflectivity or the subsequently derived conductivity of the graphene sample. More importantly, there also exists a threshold value for the photoinduced differential transmission $\Delta T|_c$ that corresponds to zero optical conductivity, above which optical gain has to emerge because of the negative conductivity:

$$\Delta T|_c = \frac{2\pi \alpha_{\text{QED}}}{n_s + 1}.$$  

(13)

From (6) to (7) it follows for the differential transmission after delay time $\tau$ that:

$$\Delta T \frac{R}{T}(\tau) = \frac{\Delta R}{R}(\tau) \frac{1 - n_s}{2}.$$  

(14)

The extracted peak transient transmission as a function of the pump fluence, as shown in figure 5(c), clearly shows the positive transmission change and, most importantly, that the critical value (blue line) for zero conductivity indeed occurs. While those data for the transmission were obtained indirectly from our reflectivity measurements, a direct measurement of the transmission would be an important confirmation of our results, ideally using large-area free-standing graphene monolayer samples.

5. Analysis of the density of transient electrons/holes

The amplitude of the time-dependent absorption $A$ as a function of pump fluence can be derived from the measured differential reflectivity by applying the Fresnel equations in the thin-film limit [2, 40]

$$\frac{\Delta A(I_p)}{A_0} = \frac{\Delta R_{g+s}(I_p)}{R_{g+s}} n_s^2 - 1 + 4A_{g,0}.$$  

(15)

The peak amplitude $A(I_p) = A_0 + \Delta A(I_p)$ gradually diminishes with increasing pump fluence. From the measured transient saturation curve above, one can extract the density of photoexcited electrons (holes) in graphene after the propagation of a single laser
pulsation of 35 fs ($\tau_p$) with a pump fluence $I_p$:

$$n_{ex}(I_p) = \int_{-\infty}^{\infty} \frac{dt}{\tau_p} n_{ex}(t, I_p) = \frac{1}{\hbar \omega_0} \int_{-\infty}^{\infty} \frac{dt}{\tau_p} I(t, I_p) A(t),$$

where $I(t, I_p)$ is the Gaussian pulse envelope $I(t, I_p) = I_p \sqrt{\frac{2m_e}{\hbar^2}} \exp\left(-\frac{4\hbar^2 z^2}{I_p^2}\right)$, normalized such that the total pulse fluence is $I_p = \int_{-\infty}^{\infty} \frac{dt}{\tau_p} I(t, I_p)$. Since $A(t) = A_0 + \Delta A(t) = A_0(1 + \frac{\Delta A(t)}{A_0})$, we have

$$n_{ex}(t, I_p) = \frac{I(t, I_p)A_0}{\hbar \omega_0} \left(1 + \frac{\Delta A(t)}{A_0}\right).$$

Applied to graphene, where $\tau_{th} \ll \tau_p$, $A(t)$ is determined by the adiabatic dependence of the absorption on the pump fluence with $I_{\text{partial}}(t, I_p) = \int_{-\infty}^{t} \frac{dt}{\tau_p} I(t', I_p)$. Consequently, equation (17) becomes

$$n_{ex}(t, I_p) = \frac{I(t, I_p)A_0}{\hbar \omega_0} \left(1 + \frac{\Delta A(I_{\text{partial}}(t, I_p))}{A_0}\right).$$

We determine $A(I_{\text{partial}})$ experimentally from the reflectivity data of figure 6(a), combined with equation (15), as discussed above. Finally, from equations (15) to (18) we have

$$n_{ex}(I_p) = \int_{-\infty}^{\infty} \frac{I(t, I_p)A_0}{\hbar \omega_0} \left[1 + \frac{\Delta R_{g+} (I_{\text{partial}}(t, I_p))}{R_{g+}} \right] \frac{n^2 - 1 + 4A_{g,0}}{4A_{g,0}} \frac{dt}{\tau_p}.$$
distribution (20). These three conditions are expressed as

\[
n_{\text{tot}} = n_+ + n_- = n_0^0 + n_0^0, \quad (21)
\]

\[
n_{\text{ex}} = n_+ - n_0^0 = n_0^0 - n_-, \quad (22)
\]

\[
n_{n_{\text{ho}}} = u - u_0^0, \quad (23)
\]

where \(n_{\text{tot}} = N_{\text{tot}}/L^2\) represents the total density of electrons in the system, \(n_{\text{ex}} = N_{\text{ex}}/L^2\) refers to the density of photoexcited carriers, \(n_u^0\) (\(n_0^0\)) indicate the electron densities in the intermediate (initially equilibrium) state, \(u\) \((u_0^0)\) represents the intermediate \((u)\) initial energy density of the whole electron system, and \(\hbar\omega\) is the pump photon energy. Applying the distribution (20) to equations (21)–(23) and taking into account the valley and spin degeneracy in graphene, we obtain the following expressions in terms of fugacities \(z_0^0 = e^{\mu_0^0/\text{hv}}\), \(z_\pm = e^{\mu_\pm/\text{hv}}\) with initial temperature \(T_0^0 = 300\text{ K}\),

\[
\delta = \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ -\text{Li}_2(-z_+^0) + \text{Li}_2 \left( -\frac{1}{z_-^0} \right) \right]
\]

\[
\delta = \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ -\text{Li}_2(-z_-^0) + \text{Li}_2 \left( -\frac{1}{z_+^0} \right) \right], \quad (24)
\]

with \(\delta\) referring to the initial doping density with respect to the neutrality point, and

\[
n_{\text{ex}} = \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ (k_B T_0^0)^2 \right] \left[ -\text{Li}_2(-z_-^0) \right]
\]

\[
- \left( k_B T_0^0 \right)^2 \left[ -\text{Li}_2(-z_+^0) \right]
\]

\[
= \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ (k_B T_0^0)^2 \right] \left[ -\text{Li}_2 \left( -\frac{1}{z_-^0} \right) \right]
\]

\[
- \left( k_B T_0^0 \right)^2 \left[ -\text{Li}_2 \left( -\frac{1}{z_+^0} \right) \right], \quad (25)
\]

as well as

\[
n_{n_{\text{ho}}} = \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ (k_B T_0^0)^2 \right] \left[ -\text{Li}_3(-z_+^0) - \text{Li}_3 \left( -\frac{1}{z_-^0} \right) \right]
\]

\[
- \left( k_B T_0^0 \right)^2 \left[ -\text{Li}_3(-z_-^0) - \text{Li}_3 \left( -\frac{1}{z_+^0} \right) \right], \quad (26)
\]

where \(g = 4\) is the flavor index taking into account the valley and spin degeneracies, \(v\) represents the Fermi velocity \(v \approx 1.1 \times 10^6\text{ m s}^{-1}(\frac{1}{\sqrt{m_e}})\) in graphene, and the polylogarithm is defined by a power series \(\text{Li}_n(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^n}\). Solving the three equations gives the transient electron temperature \(T_e\) and the individual chemical potentials \(\mu_\pm = k_B T_e \ln z_\pm\) at a given photoexcitation density \(n_{\text{ex}}\) with initial temperature \(T_0^0\) and initial chemical potential \(\mu^0\) associated with the equilibrium state before being excited.

To perform the numerical calculation, we introduce the dimensionless variables

\[
f_{\text{ex}} = \frac{n_{\text{ex}}}{\bar{n}}, \quad x = \frac{\delta}{\bar{n}}, \quad t_e = \frac{k_B T_e}{D}, \quad (27)
\]

\[
x = \frac{\mu_{\pm}}{D}, \quad \Omega = \frac{\hbar\omega}{D}, \quad (28)
\]

with a choice for the upper momentum cutoff \(\Lambda\) to define the energy scale \(D = \text{hv}\Lambda\) and the density scale \(\bar{n} = \frac{\Lambda^2}{\pi}\).

Here we choose \(\Lambda = \frac{\pi}{2}(2\pi/\Lambda)^2/\Lambda_0\), where \(\Lambda_0 = 3^3/2^6 \xi/2\) is the area of the hexagonal unit cell. Note that these dimensionless units are solely introduced for computational convenience. None of our final expressions depends on the actual values of \(\Lambda, D\) or \(\bar{n}\), as these quantities cancel in the final results (see for example equation (34)). In terms of the dimensionless variables, the equations are expressed as

\[
f_{\text{ex}} - 1 = x = \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ -\text{Li}_2(-z_+^0) + \text{Li}_2 \left( -\frac{1}{z_-^0} \right) \right] + \left( k_B T_0^0 \right)^2 \left[ -\text{Li}_2(-z_-^0) + \text{Li}_2 \left( -\frac{1}{z_+^0} \right) \right], \quad (28)
\]

and

\[
f_{\text{ex}} = \frac{g}{2\pi} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ -\text{Li}_2(-z_+^0) + \text{Li}_2 \left( -\frac{1}{z_-^0} \right) \right] + \left( k_B T_0^0 \right)^2 \left[ -\text{Li}_2(-z_-^0) + \text{Li}_2 \left( -\frac{1}{z_+^0} \right) \right], \quad (29)
\]

as well as

\[
f_{\text{ex}} = \frac{g}{\Omega} \left( \frac{k_B T_0^0}{\text{hv}} \right)^2 \left[ -\text{Li}_3(-z_+^0) - \text{Li}_3 \left( -\frac{1}{z_-^0} \right) \right] + \left( k_B T_0^0 \right)^2 \left[ -\text{Li}_3(-z_-^0) - \text{Li}_3 \left( -\frac{1}{z_+^0} \right) \right], \quad (30)
\]

In the following analysis, either equation set (24)–(26) or the set (28)–(30) will be employed for convenience.

6.2. Characteristics of the intermediate electronic state

We carry out our analysis for two cases: undoped graphene, i.e., the system at the charge neutrality point, and graphene on a SiC substrate with a finite electron doping. It is easy to show that the hole-doped system is symmetric to the electron-doped system. By solving for the electron temperature \(T_e\) and the chemical potentials \(\mu_\pm\) at different photoexcitation densities, we demonstrate the characteristics of this intermediate electronic state.

6.2.1. Neutral system. The simplest case is the system at the neutrality point, i.e., \(\delta = 0\), possessing particle–hole symmetry. Equation (28) yields \(z_\pm^0 = 1(\mu_\pm = 0)\) and \(z_+ = \frac{1}{2} = z(\mu_+ = -\mu_- = \mu)\), i.e., the lower-band chemical potential is always the opposite of the upper-band one in the neutral system. From equations (29) to (30), we obtain the expression for the dimensionless temperature \(t_e\):

\[
t_e = \left( \frac{\mu_{\pm}^0 + (\mu_{\pm}^0)^2 \pi^2}{\text{hv}} \right)^{1/2}, \quad (31)
\]

and the relation

\[
h(z) = \left( \frac{\mu_{\pm}^0 + (\mu_{\pm}^0)^2 \pi^2}{\text{hv}} \right)^{3/2}, \quad (32)
\]
For instance, at low photoexcitation density $n$, the system is rapidly heated up at lower densities, but is slowly cooled at high densities.

Figure 7. Electron temperature $T_e$ as a function of the photoexcitation density $n_{ex}$ in the neutral system. We can see that the system is rapidly heated up at lower densities, but is slowly cooled at higher densities.

Figure 8. Plot of the upper-band chemical potential $\mu_+$ ($n_{ex}$), in units of eV, in the neutral system. The lower-band chemical potential $\mu_- = -\mu_+$. Clearly, the upper-band chemical potential becomes negative at low densities before rising to become positive at high densities.

$$h(z) = \frac{[-L_2(-z)]^{3/2}}{L_2(-z)}.$$  \hspace{1cm} (33)

Since $h(z)$ is monotonically increasing with an upper bound $3/\sqrt{2}$ in the large $z$ limit, it implies a maximum value of $f_{ex}$:

$$f_{ex}^{\text{max}} = \left(\frac{9}{16\pi^2}\right)^{\frac{1}{2}}.$$  \hspace{1cm} (34)

For instance, at $\hbar \omega = 1.55$ eV the phase space capacity becomes $n_{ex}^{\text{max}} = 9.7779 \times 10^{13}$ cm$^{-2}$. In this limit, the electron temperature approaches zero as $z \rightarrow \infty$, $t_e \rightarrow (\hbar \omega)^{1/2} = \frac{3\Omega}{4\pi} \rightarrow 0$.

For a 800 nm pump with photon energy $\hbar \omega = 1.55$ eV, solving equations (31) and (32), we obtain $T_e$ as a function of $n_{ex}$, as plotted in figure 7. It shows that the electron temperature rises rapidly at low photoexcitation densities, but, instead of remaining heated up, it starts slowly cooling at higher densities, eventually approaching zero at a maximal density.

The value of $\mu$ with respect to $n_{ex}$ is plotted in figure 8. We clearly see that it becomes negative at low photoexcitation densities during the period of rapid heating, but returns to positive as the temperature slowly decreases.

The down-turn behavior in electron temperature and the negative-to-positive transition in chemical potential signifies a crossover behavior, indicating that at a small pump fluence the excited carriers form a hot and dilute classical gas, but as more carriers are excited they gradually build up a quantum degenerate fermion system with the temperature cooling down in order to accommodate more electrons in the finite phase space. If the phase space could really be exhausted, the electron- and hole-carriers would be pumped into zero-temperature Fermi–Dirac distributions in which the carriers are closely packed with a sharp Fermi edge.

6.2.2. Exhaustion of phase space. Inspired by the analysis of the neutral system, we see that phase space capacity is exhausted at zero electron temperature. To obtain an analytical estimate of the maximal available phase space at different electron-doping levels, we assume the initial temperature to be zero for convenience. Equations (21)–(23) are then simplified as

$$\delta = \frac{1}{\pi} \frac{1}{(\hbar \omega)^2} [\mu_{+}^{\text{max}}]^2 - (\mu_{-}^{\text{max}})^2] = \frac{1}{\pi} \frac{1}{(\hbar \omega)^2} (\mu_{+}^{0})^2,$$  \hspace{1cm} (35)

$$n_{ex}^{\text{max}} = \frac{1}{\pi} \frac{1}{(\hbar \omega)^2} [\mu_{+}^{\text{max}}]^2 - (\mu_{-}^{\text{max}})^2] = \frac{1}{\pi} \frac{1}{(\hbar \omega)^2} (\mu_{+}^{0})^2,$$  \hspace{1cm} (36)

$$n_{ex}^{\text{max}} \hbar \omega = \frac{2}{3\pi} \frac{1}{(\hbar \omega)^2} [\mu_{+}^{\text{max}}]^3 + (-\mu_{-}^{\text{max}})^3 - (\mu_{+}^{0})^3].$$  \hspace{1cm} (37)

In terms of the dimensionless variables defined in (27), we find a relation between the maximal photoexcitation density and the doping level from the above equations

$$f_{ex}^{\text{max}} = \frac{2}{3\Omega} [(f_{ex}^{\text{max}} + \chi)^{3/2} + (f_{ex}^{\text{max}})^{3/2} - \chi^{3/2}].$$  \hspace{1cm} (38)

Solving this equation yields $n_{ex}^{\text{max}}$ at different doping densities, as shown in figure 9.
then the coupled equations are reduced to

\[ \text{with} \]

\[ \text{As seen from equation (34) for the neutral system, } n_{\text{ex}}^{\text{max}} \sim \frac{\mu^0}{\beta}, \text{ the available phase space rises with increasing pump frequency. On the other hand, phase space capacity decreases with increasing initial electron-doping density, as expected.}

However, for the photoexcitation density \( n_{\text{ex}} \) as an input parameter in our calculation, a critical question to ask is: does this maximal density \( n_{\text{ex}}^{\text{max}} \) equal the saturation density \( n_{\text{sat}}^{\text{max}} \) in a real pumping process, or in other words, can phase space be completely filled? We will answer this question later.

### 6.2.3. Doped system

Next we discuss the system away from the Dirac point with a finite electron doping, i.e., \( \delta = 0 \) or \( x = \frac{\delta}{\beta} \geq 0 \), which is often the case, e.g., in epitaxial graphene on a SiC substrate. In this case, from equations (28) to (30) we obtain the expression of \( t_e \) as a function of \( z_+ \)

\[ t_e = \left( \frac{\frac{\Delta_0}{2} + (\Omega_0^2)^{1/2}[\text{Li}_2(-z_+)]}{-\text{Li}_2(-z_+)} \right)^{1/2}, \quad (39) \]

then the coupled equations are reduced to

\[ \text{with} \]

\[ (\text{40}) \]

\[ (\text{41}) \]

\[ \text{Solving the two equations (40) and (41) we obtain } z_+ \text{ and } z_-, \text{ which in turn gives } t \text{ via equation (39). Finally, the physical quantities are derived through } k_B T_e = t_e D, \mu_+ = t_e D \ln z_+, \mu_- = t_e D \ln z-. \]

The evolution of electron temperature with photoexcitation density is smoother compared to the neutral system.

To show the numerical results, we choose the experimental system of graphene on SiC substrate with an initial electron doping \( \delta = 1.17 \times 10^{13} \text{ cm}^{-2} \), corresponding to an initial chemical potential \( \mu^0 = 0.4 \text{ eV} \), being excited by the pump energy \( h\omega = 1.55 \text{ eV} \). The phase space capacity is calculated from equation (38) to be \( n_{\text{ex}}^{\text{max}} = 8.34 \times 10^{13} \text{ cm}^{-2} \) at this doping level. The electron temperature \( T_e \) (in units of kelvin) changing with \( n_{\text{ex}} \) (in units of \( 10^{13} \text{ cm}^{-2} \)) is plotted in figure 10. Compared to the undoped system, the evolution of electron temperature with photoexcitation density is smoother and the electron temperature is lower due to the finite initial carrier density.

Figure 11 shows the upper- and lower-band chemical potentials \( \mu_+ \) and \( \mu_- \) (in units of eV) varying with \( n_{\text{ex}} \) (in units of \( 10^{13} \text{ cm}^{-2} \)).

Clearly, due to the large initial electron doping, the low-density classical gas phase for the upper-band electrons is now absent, although there is a tiny presence for the lower band. In the doped case, the upper- and lower-band chemical potentials are not symmetric, \( \mu_+ \neq -\mu_- \), as they are in the neutral system. The separation between the two chemical potentials increases with photoexcitation density.

### 6.2.4. Broadband distribution and blue-shifted photoluminescence

A direct consequence of the high electron temperature \( T_e \sim 3000-4000 \text{ K} \) and the slow population relaxation is a broadband distribution of electron and hole excitations. This can be seen in the occupation number \( N_{e,h}(\epsilon) = D(\epsilon)/f_{e,h}(\epsilon) \), where \( D(\epsilon) = \frac{2e}{\pi h^2} \) is the density of states at energy \( \epsilon \), and \( f_{e,h}(\epsilon) \) are the electron and hole distribution functions with \( f_e = f_+ \), \( f_h = 1 - f_- \). Figure 12 shows the electron and hole distribution at different photoexcitation densities in the neutral system and in the electron-doped system (\( \mu^0 = 0.4 \text{ eV} \)).
By analyzing its behavior at high densities, for the nonequilibrium intermediate state using the Keldysh formalism, we calculate the optical conductivity responses of this electronic state at different photoexcitation densities. In this section, we calculate the optical conductivity observable in experiments. The high-temperature tail in the distribution extends for up to 2–3 eV. This coverage of higher energy states enables the excited carriers well above the excitation energy 1.55 eV, modification of the spectrum.

The optical conductivity is used in the spectral functions to avoid an artificial connection between the real part of conductivity and the nonequilibrium state, but an average chemical potential is employed in the distribution functions to characterize the nonequilibrium state, where \( \sigma_{y,z} \) are Pauli matrices due to the chiral structure of the Dirac fermions in graphene. Note that we set \( \hbar \equiv 1 \) during the derivation, but will recover it in the final results.

In the Keldysh formalism, the bubble diagram contributing to the optical conductivity gives the real part as

\[
\text{Re } \sigma_{\alpha\beta}(\omega) = \frac{g\pi}{\omega} \int \frac{d\omega'}{(2\pi)^2} \left[ \text{Tr} \hat{j}_{\alpha k} \hat{\Lambda}_k(\omega' + \omega) \hat{j}_{\beta k} \hat{N}_k(\omega') \right. \\
\left. - \hat{j}_{\alpha k} \hat{\Lambda}_k(\omega' + \omega) \hat{j}_{\beta k} \hat{N}_k(\omega + \omega) \right] 
\]

for the direction \( \alpha(\beta) = x, y \) in the 2D graphene layer with the definitions

\[
\hat{\Lambda}_k(\omega) = \frac{i}{2\pi} (\hat{G}_k^{\text{ret}}(\omega) - \hat{G}_k^{\text{adv}}(\omega)), \\
\hat{N}_k(\omega) = -\frac{i}{2\pi} \hat{G}_k^{\text{ret}}(\omega). 
\]

Here the retarded and advanced Green’s functions are matrices in the band representation

\[
\hat{G}_k^{\text{ret/adv}}(\omega) = \begin{pmatrix} 1 & 0 \\ \omega \pm i0^+ + \hat{\mu} - \nu k & 1 \end{pmatrix} 
\]

where the \( + (\text{\ or\ } -) \) sign is associated with the retarded (advanced) Green’s function, and the lesser Green’s function is written as

\[
\hat{G}_k^{\text{<}}(\omega) = \begin{pmatrix} g_k^{<}(\omega) & 0 \\ 0 & g_k^{>}(\omega) \end{pmatrix}, \\
g_k^{<}(\omega) = 2\pi i f(\epsilon_\pm(k) - \hat{\mu}) \delta(\omega - \epsilon_\pm(k) + \hat{\mu}),
\]

with \( \hat{\mu} = \frac{1}{2} (\mu_+ + \mu_-) \) and the Fermi function \( f(x) \equiv \frac{1}{e^{x/T} + 1} \). Note that distinct chemical potentials are employed in the distribution functions to characterize the nonequilibrium state, but an average chemical potential is used in the spectral functions to avoid an artificial modification of the spectrum.

Previous analysis (see section 3) shows that the optical properties of graphene on an insulating substrate, such as reflection, transmission, and absorption, are naturally explained in our model.
From equation (46) we calculate the longitudinal conductivity, which contains intraband and interband transitions. To show the transition processes specifically, introduce $a_{\lambda \lambda}(\omega) \equiv \delta(\omega - \lambda \nu + \bar{\mu})$, and $f_{\lambda}(\omega) \equiv f(\omega - \lambda \nu \mu)$. It follows that the intraband and interband conductivities are

$$
\text{Re} \sigma_{xx}^{\text{intra}}(\omega) = g \pi \langle ev \rangle^2 \int \frac{d\omega}{(2\pi)^2} d^2 k \cos^2 \theta \\
\times \sum_{\lambda = \pm} a_{\lambda \lambda}(\omega') a_{\lambda \lambda}(\omega' + \omega) \\
\times f_{\lambda}(\omega') - f_{\lambda}(\omega' + \omega),
$$

(52)

$$
\text{Re} \sigma_{xx}^{\text{inter}}(\omega) = g \pi \langle ev \rangle^2 \int \frac{d\omega}{(2\pi)^2} d^2 k \sin^2 \theta \\
\times \sum_{\lambda = \pm} a_{\lambda \lambda}(\omega') a_{\lambda \lambda}(\omega' + \omega) \\
\times f_{\lambda}(\omega') - f_{\lambda}(\omega' + \omega) \omega \\
(53)
$$

where $\cos \theta = \frac{k}{\bar{\nu}}$, $\sin \theta = \frac{k}{\bar{\nu}}$.

6.3.2. Intraband transition. First let us evaluate intraband conductivity. It is straightforwardly obtained from equation (52)

$$
\text{Re} \sigma_{xx}^{\text{intra}}(\omega) = \frac{g \langle ev \rangle^2}{(2\pi)^2} \delta(\omega) \int_0^\infty k \, dk \\
\times \left[ - \frac{\partial f(\omega)}{\partial \omega} \bigg|_{\omega = \nu k - \mu_+} - \frac{\partial f(\omega)}{\partial \omega} \bigg|_{\omega = \nu k - \mu_-} \right] \\
= \frac{e^2}{h} \ln[(1 + z_+)(1 + z_-)] k_B T_e \delta(\omega)
$$

(54)

where we have recovered the factor $h$ on the last line. The delta-function will be replaced by a Lorentzian $\delta(\omega) \rightarrow \frac{1}{\omega^2 + \epsilon^{-1}}$ for further discussions, which is not our concern here. In the equilibrium state $z_+ = z_- = z_0 = e^{\beta \mu_0}$, the intraband conductivity becomes $\text{Re} \sigma_{xx}^{\text{intra}}(\omega) = \frac{e^2}{\hbar} k_B T_e \ln(2 + e^{\beta \mu_0} + e^{-\beta \mu_0}) \delta(\omega)$, which recovers the well-known expression in the neutral system at equilibrium.

The most interesting observation from the intraband transition for the transient electronic state is the modified Drude spectral weight

$$
D = \frac{e^2}{\hbar} \ln[(1 + z_+)(1 + z_-)] k_B T_e,
$$

(55)

which can be significantly enhanced by the high electron temperature. But it could also be reduced when the reduction of chemical potential dominates at low densities in the neutral system. Here we show the Drude weight change, normalized by the equilibrium value $D_0 = \frac{e^2}{\hbar} \ln[(1 + z_0)(1 + 1/z_0)] k_B T_e$, at different $n_{xx}$ in the neutral and electron-doped systems in figure 13.

The results for the neutral system exhibit a drop in the Drude spectral weight at low densities due to the large drop in chemical potential, as shown in figure 8, but this is quickly followed by large enhancement at higher densities. In the electron-doped system, the Drude weight is always increasing, but with much less enhancement than in the neutral system.

6.3.3. Interband transition. In order to understand the optical response at high frequencies, as the optical conductivity is dominated by the interband transition for frequencies on the order of 1 eV, we evaluate the interband conductivity from equation (53),

$$
\text{Re} \sigma_{xx}^{\text{inter}}(\omega) = \frac{g \langle ev \rangle^2}{(2\pi)^2} \left[ f \left( \frac{\omega}{2} - \mu_- \right) - f \left( \frac{\omega}{2} - \mu_+ \right) \right] \\
= \frac{e^2}{4\hbar} \left[ \tanh \left( \frac{\hbar \omega + 2\mu_-}{4k_B T_e} \right) \\
+ \tanh \left( \frac{\hbar \omega - 2\mu_+}{4k_B T_e} \right) \right]
$$

(56)

where the probe photon frequency $\omega > 0$ and we have reinserted the factor $h$ on the last line. In the equilibrium state, $\mu_+ = \mu_- = \mu_0$, the interband transition becomes...
Re $\sigma_{\text{inter}}^{\text{neural system}}(\omega) = \frac{e^2}{\hbar} \left[ \tanh \left( \frac{\hbar \omega + 2\mu^0}{4\hbar k_B T} \right) + \tanh \left( \frac{\hbar \omega - 2\mu^0}{4\hbar k_B T} \right) \right]$, which gives the expression for the neutral system in equilibrium

$\text{Re } \sigma_{\text{ex}}^{\text{inter}}(\omega) = \frac{e^2}{\hbar} \tanh \left( \frac{\hbar \omega}{4\hbar k_B T} \right)$, as expected.

By studying the optical response to different photon energies at various photoexcitation densities, unusual optical properties of the transient electronic state are found, which will be discussed in the following.

**Femtosecond absorption saturation and perfect transparency.**

Let us first consider the optical response to the pump frequency. An interesting observation from the interband transition formula (56) arises due to the two density-dependent chemical potentials. As shown in figures 8 and 11, with increasing photoexcitation density the separation of the two chemical potentials also becomes larger. Then, at a certain photoexcitation density such that

$$\mu_+ - \mu_- = \hbar \omega,$$

the optical conductivity vanishes and the system becomes perfect transparent. For higher densities, $\mu_+ - \mu_- > \hbar \omega$, such that the optical conductivity becomes negative, which implies a stimulated emission to keep the photoexcitation density from rising. This indicates that the absorption becomes zero and the number of excited carriers saturates at this density $n_{\text{ex}}^{\text{sat}}$, stabilized by the stimulated emission.

To show the variation of optical conductivity with photoexcitation density, we perform calculations for the neutral system and the electron-doped system with initial doping $\mu^0 = 0.4$ eV by applying a pump photon energy at $\hbar \omega = 1.55$ eV. We show the results in figure 14, where they are normalized by the equilibrium value $\sigma_0 = \frac{e^2}{4\hbar}$.

In both cases, the conductivity monotonously decreases due to the increasing electron temperature and separation of the chemical potentials. The neutral system saturates at $n_{\text{ex}}^{\text{sat}}(\text{theory}) = 5.7 \times 10^{13}$ cm$^{-2}$, while the electron-doped system saturates at roughly $n_{\text{ex}}^{\text{sat}}(\text{theory}) = 4.8 \times 10^{15}$ cm$^{-2}$. On the other hand, the experimental measurement of the electron-doped system gives $n_{\text{ex}}^{\text{sat}}(\text{expt.}) = 5.0 \times 10^{13}$ cm$^{-2}$, as shown in figure 6(b), which is in excellent agreement with the theoretical value $4.8 \times 10^{13}$ cm$^{-2}$. This corroborates the correct description of the transient electronic state in our model. And it also answers the earlier posed question: the system saturates at a lower photoexcitation density before completely filling the available phase space, i.e., $n_{\text{ex}}^{\text{sat}} < n_{\text{ex}}^{\text{max}}$.

This theoretical calculation of the optical gain can serve as a test of our model, which has been used to simulate the optical differential reflectivity data performed in figure 5(b) (red line). The agreement is excellent.

**Femtosecond stimulated emission and optical gain.**

It is easy to see that a higher-frequency pump will saturate at a higher density since it can open up more phase space. Then when applying a probe with a frequency higher than the pump frequency, we will expect that it cannot detect the zero absorption, as long as it is still within the low-energy Dirac spectrum, as shown in figure 15 (green line). However, if one applies a lower-frequency probe, but not so low that it is still mainly detecting the change in the interband transition, one would expect an optical gain in the vicinity of the saturation density, as the optical conductivity becomes negative in this regime, as shown in figure 15 (blue line, yellow region). The appearance of negative conductivity signifies a stimulated emission that drives the system to a lower density, as illustrated in figure 2. We stress that the transient conductivity is negative in a regime below the pump frequency but above a certain frequency below which the intraband transition becomes dominant.

**Comparison of two model calculations with pump–probe spectroscopy measurements.**

Here we further compare the calculated optical conductivity from the distinct-$\mu$ model ($\mu_+ \neq \mu_-$) discussed above and the equal-$\mu$ model ($\mu_+ = \mu_-$) with the experimental value measured at probe photon energies $\hbar \omega = 1.55$ and 1.16 eV for a pump energy at $\hbar \omega = 1.55$ eV. As shown in figure 16, we compare the experimentally-extracted, transient conductivity at 40 fs [18] with the calculated conductivity $\sigma(\omega)$ as a function of the photoexcited carrier density $n_{\text{ex}}$ for two probe photon energies 1.55 and 1.16 eV. The Fermi energy of the sample is $\sim 0.4$ eV. The model calculation with the distinct chemical potentials reproduces the salient features of the experiment, including nonlinear saturation and optical gain. Excellent agreement between experiment and theory also demonstrates a faithful representation of the transient state at 40 fs by the model.
Figure 15. The calculated interband conductivity $\frac{\sigma(\omega)}{\sigma_0}$, normalized by the equilibrium value $\sigma_0 = \frac{e^2}{4\hbar}$, at a higher frequency ($\bar{h}\omega = 1.7$ eV, green line), the pump frequency ($\bar{h}\omega = 1.55$ eV, magenta line), and a lower frequency ($\bar{h}\omega = 1.2$ eV, blue line). It shows that in the vicinity of the saturation density the optical conductivity at lower frequencies (but still high enough to mainly detect interband transitions) becomes negative. This indicates a stimulated emission that enables an optical gain for low-frequency probes. All of these results agree quantitatively with the experimental values of $5.0 \times 10^{13}$ cm$^{-2}$ and $3.4 \times 10^{13}$ cm$^{-2}$, respectively.

7. Conclusions

We have studied the electronic states in photoexcited graphene formed via rapid carrier–carrier scattering after strong photoexcitation but before the energy relaxation that takes place on a longer time scale. We have provided evidence for the existence of pronounced femtosecond population inversion and broadband gain in strongly photoexcited graphene monolayers. These results clearly reveal the transient electron and hole potentials are separated on a time scale of hundreds of femtoseconds. By characterizing the state in terms of two separate Fermi–Dirac distributions with a common electron temperature but distinct chemical potentials for the upper and lower bands, we showed that this intermediate electronic state is associated with a high electron temperature $T_e$ of up to 3000–4000 K, which causes a broadband distribution extended to higher energy and is responsible for the observed blue-shifted photoluminescence component. Our analysis on the variation of electron temperature and chemical potentials with photoexcited carrier density in the neutral system clearly shows a crossover from a hot dilute classical gas to dense quantum degenerate fermions. And, unlike the phase space restriction in most semiconductors for a pump pulse on the order of 10 fs, which is determined by the density of states at the optical excitation and the frequency width of the pulse, the fast depletion of phase space in graphene yields a broadband filling which significantly increases the accommodation of photoexcited carriers.

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