In the past two years a great deal of attention has been attracted by a recently discovered, new two-dimensional (2D) electronic system —graphene, built out of a single monolayer of carbon atoms with a honeycomb 2D crystal structure [1,2]. The band structure of the charge carriers in this system consists of six Dirac cones at the corners of the hexagon-shaped Brillouin zone [3,4], with the massless, linear electron/hole dispersion (only one third of each cone belongs to the first Brillouin zone, therefore one can also talk about two (independent) Dirac cones in graphene). The massless electron spectrum leads to unusual transport and electrodynamic properties, which have been intensively studied in the literature, see, e.g., [5–35] and for review [36,37].

Electrodynamic properties of graphene have been theoretically studied in refs. [16–33]. The frequency-dependent conductivity [16–18,21–24], as well as plasmon [25,27,29, 31,32], plasmon-polariton [26], and transverse electromagnetic wave spectra [33] have been investigated. In all these papers electrodynamic response of the system has been studied within the *linear response* theory (for instance, using the Kubo formalism, or the random phase approximation, or the self-consistent-field approach). In this letter we show that, apart from all the fascinating and non-trivial properties of graphene predicted and observed so far, this material should also demonstrate *strongly non-linear* electrodynamic behavior. In particular, irradiation of the graphene sheet by a harmonic electromagnetic wave with frequency Ω should lead to the emission of the higher harmonics with frequencies $m\Omega$, $m = 3, 5, \ldots$, from the system. The operating frequency of such a frequency multiplier can vary from microwaves up to infrared, and

the required ac electric field is rather low, especially at low carrier densities and low temperatures. The predicted non-linear electrodynamic properties of graphene may open up new exciting opportunities for building electronic and optoelectronic devices based on this material.

To qualitatively demonstrate the non-linear behavior of graphene electrons, consider a classical 2D particle with charge $-e$ and energy spectrum $\epsilon_{\mathbf{p}} = Vp = V\sqrt{p_x^2 + p_y^2}$ in the external electric field $E_x(t) = E_0\cos\Omega t$. Here V is the velocity of 2D electrons in the energy band (in graphene $V \approx 10^8$ cm/s [1,2]). According to the classical equations of motion $\mathrm{d}p_x/\mathrm{d}t = -eE_x(t)$, the momentum p_x will then be equal to $p_x(t) = -(eE_0/\Omega)\sin\Omega t$, and the velocity $v_x = \partial\epsilon_{\mathbf{p}}/\partial p_x$ is then $v_x(t) = -V\,\mathrm{sgn}(\sin\Omega t)$. If there are n_s particles per unit area, the corresponding ac electric current,

$$j_x(t) = en_s V\,\mathrm{sgn}(\sin\Omega t) =$$
$$en_s V\frac{4}{\pi}\left\{\sin\Omega t + \frac{1}{3}\sin 3\Omega t + \frac{1}{5}\sin 5\Omega t + \ldots\right\}, \quad (1)$$

contains all odd Fourier harmonics, with amplitudes j_m, $m = 1, 3, 5, \ldots$, falling down very slowly with the harmonics number, $j_m \sim 1/m$. Notice that at the density $n_s = 6 \cdot 10^{12}$ cm^{-2} and at $V \simeq 10^8$ cm/s (parameters of refs. [1,2]) the current amplitude $j_0 = en_s V$ in our simple estimate gives a giant value of $j_0 \simeq 100$ A/cm.

The above consideration does not take into account the Fermi distribution of charge carriers over the quantum states in the conduction and valence bands of graphene. To get a more accurate description of the non-linear phenomena in the considered system, we use the kinetic
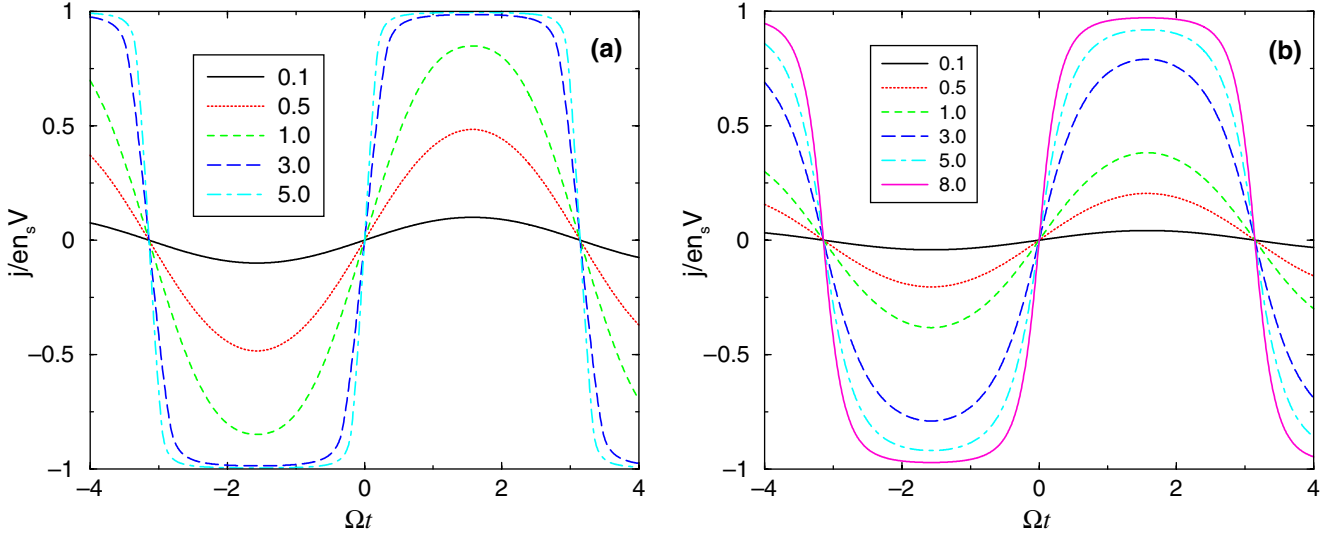
Fig. 1: (Color online) The time dependence of the ac electric current, measured in units en_sV, at harmonic excitation of the system at frequency Ω. (a) The temperature is zero, $T/\epsilon_F = 0$; the curves are labeled by the values of the electric-field parameter $Q_{F0} = eE_0V/\Omega\epsilon_F$. (b) The temperature is finite, the Fermi energy is zero, $\epsilon_F = 0$; the curves are labeled by the values of the parameter $Q_{T0} = eE_0V/\Omega T$.

Boltzmann theory, which allows one to get an exact response of the system not imposing any restrictions on the amplitude of the external ac electric field $\mathbf{E}(t)$. Using this quasi-classical approach, we take into account the intra-band contribution to the ac electric current. The inter-band contribution to the electric current, due to the transitions between the hole and the electron bands, is ignored. This imposes certain restrictions on the frequency of radiation Ω, which will be discussed below.

Consider a 2D electron/hole gas with the energy spectrum $\epsilon_{\mathbf{p}\pm} = \pm V\sqrt{p_x^2 + p_y^2}$ under the action of the field $\mathbf{E} = (E_x, 0)$, where the sign $+$ $(-)$ corresponds to the electron (hole) band, $E_x(t) = E_0 e^{\alpha t}\cos(\Omega t)$, and $\alpha \to +0$ describes an adiabatic switching-on of the electric field. Assume that the Fermi energy ϵ_F lies in the electron (or the hole) band and that the temperature is small as compared to ϵ_F, $T \ll \epsilon_F$. The momentum distribution function of electrons $f_{\mathbf{p}+}(t) \equiv f_{\mathbf{p}}(t)$ (we omit the sign $+$ for brevity) in the collisionless approximation is described by the Boltzmann equation

$$\frac{\partial f_{\mathbf{p}}(t)}{\partial t} - \frac{\partial f_{\mathbf{p}}(t)}{\partial p_x}eE_0 e^{\alpha t}\cos(\Omega t) = 0, \qquad (2)$$

which has the exact solution

$$f_{\mathbf{p}}(t) = F_0(p_x - p_0(t), p_y), \qquad (3)$$

where

$$F_0(p_x, p_y) = \left[1 + \exp\left(\frac{V\sqrt{p_x^2 + p_y^2} - \epsilon_F}{T}\right)\right]^{-1} \qquad (4)$$

is the electronic Fermi function, and $p_0(t) = -(eE_0/\Omega)e^{\alpha t}\sin\Omega t$ is the solution of the single-particle

equation of motion. The electric current $\mathbf{j}(t) = -eg_s g_v S^{-1}\sum_{\mathbf{p}}\mathbf{v}f_{\mathbf{p}}(t)$ then assumes the form

$$j_x(t) = -\frac{g_s g_v eV}{(2\pi\hbar)^2}\iint \mathrm{d}p_x \mathrm{d}p_y \frac{p_x}{\sqrt{p_x^2 + p_y^2}}$$
$$\times F_0(p_x - p_0(t), p_y), \qquad (5)$$

$j_y = 0$, where $g_s = g_v = 2$ are the spin and valley degeneracies in graphene, and S is the sample area. After some lengthy but simple transformation, eq. (5) can be rewritten as

$$j_x(t) = en_s V \frac{4}{\pi}\frac{2Q_F(t)}{\sqrt{1 + Q_F^2(t)}}$$
$$\times \int_0^{\pi/2}\frac{\cos^2 x\,\mathrm{d}x}{\sqrt{1 + \frac{2Q_F(t)}{1+Q_F^2(t)}\cos x} + \sqrt{1 - \frac{2Q_F(t)}{1+Q_F^2(t)}\cos x}}, \qquad (6)$$

where

$$n_s \equiv n_e = \frac{g_s g_v p_F^2}{4\pi\hbar^2} = \frac{g_s g_v \epsilon_F^2}{4\pi\hbar^2 V^2} \qquad (7)$$

is the density of electrons, $p_F = \epsilon_F/V$ is the Fermi momentum, and

$$Q_F(t) = -\frac{p_0(t)}{p_F} = \frac{eE_0 V}{\Omega\epsilon_F}\sin(\Omega t) \equiv Q_{F0}\sin(\Omega t) \qquad (8)$$

is the field parameter, proportional to the ac electric field E_0.

Figure 1(a) shows the current (6) as a function of time Ωt. One sees that in the low-field limit the response is

linear. Expanding the current (6), we get at $Q_{F0} \ll 1$

$$j_x(t) \approx en_s V Q_{F0} \left\{ \left(1 - \frac{3}{32} Q_{F0}^2 \right) \sin \Omega t + \frac{1}{32} Q_{F0}^2 \sin 3\Omega t \right\},$$ (9)

so that the linear response conductivity (in the collisionless approximation) is

$$\sigma_{\epsilon_F, T=0}(\Omega) = \frac{in_s e^2 V}{\Omega p_F} = i \frac{e^2}{\hbar} \frac{g_s g_v}{4\pi} \frac{\epsilon_F}{\hbar \Omega}.$$ (10)

Expression (10) coincides with the intra-band Drude conductivity, which can be obtained from the linear-response theory [17,18,21–23,33]. As the inter-band conductivity is of order of $e^2/\hbar$ [17,18,21–23,33], our quasi-classical approach is valid at $\hbar\Omega \lesssim \epsilon_F$. At the electron density $\simeq 10^{11}$–10^{12} cm^{-2} this restricts the frequency by the value of 10–30 THz.

In the strong-field limit $Q_{F0} \gtrsim 1$ eq. (6) results in formula (1). From the condition $Q_{F0} \gtrsim 1$, rewritten as

$$E_0 \gtrsim \frac{2\hbar\Omega\sqrt{\pi n_s}}{e\sqrt{g_s g_v}},$$ (11)

one sees that the required ac electric field grows linearly with the electromagnetic wave frequency and is proportional to the square root of the electron density. At $f \simeq 50$ GHz and $n_s \simeq 10^{11}$ cm^{-2}, the inequality (11) is fulfilled at $E_0 \gtrsim 100$ V/cm. This value can be reduced in systems with lower electron/hole density. Therefore, we consider now an opposite limiting case with $\epsilon_F = 0$, but finite temperature T.

At finite T and the vanishing $\epsilon_F = 0$ both electrons and holes contribute to the charge carrier density

$$n_s = n_e + n_h = \frac{\pi g_s g_v T^2}{12\hbar^2 V^2}$$ (12)

and to the current. Starting again from eq. (5) but accounting for the hole contribution and putting $\epsilon_F = 0$, we get

$$j_x(t) = en_s V \frac{12}{\pi^3} \int_0^\infty x \, dx$$
$$\times \int_0^\pi d\theta \frac{\cos\theta}{1 + \exp\left(\sqrt{x^2 + Q_T^2(t) - 2xQ_T(t)\cos\theta}\right)},$$ (13)

where

$$Q_T(t) = -\frac{V p_0(t)}{T} = \frac{eE_0 V}{\Omega T} \sin \Omega t \equiv Q_{T0} \sin \Omega t.$$ (14)

Figure 1(b) shows the current (13) as a function of time Ωt. In the low-field limit $Q_{T0} \ll 1$ we get from (13) the current

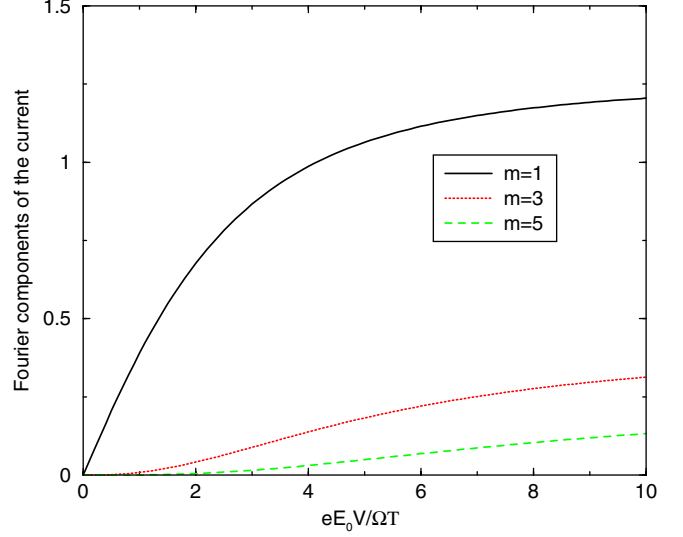$$j_x(t) \approx en_s V Q_T(t) \frac{6 \ln 2}{\pi^2},$$ (15)

Fig. 2: (Color online) The Fourier components of the current (13) as a function of $Q_{T0} = eE_0 V/\Omega T$ at $\epsilon_F/T = 0$.

and the correct expression for the linear-response intra-band dynamic conductivity [18],

$$\sigma_{\epsilon_F=0, T}(\Omega) = \frac{6 \ln 2}{\pi^2} \frac{in_s e^2 V^2}{T\Omega} = i \frac{\ln 2}{2\pi} \frac{e^2}{\hbar} \frac{g_s g_v T}{\hbar\Omega}.$$ (16)

One sees that the quasi-classical approach is now valid at $\Omega \lesssim T$. This restricts the frequency by the value of $\simeq 200$ GHz at $T \sim 10$ K and $\simeq 6$ THz at room temperature. In the strong-field regime $Q_{T0} \gtrsim 1$ eq. (13) is reduced, again, to (1). Figure 2 shows the Fourier components of the ac electric current, for $m = 1, 3$ and 5, as a function of the field parameter $eE_0 V/\Omega T$ at $\epsilon_F = 0$. The strong-field condition now assumes the form

$$E_0 \gtrsim \frac{\Omega T}{eV}.$$ (17)

At $T \simeq 10$ K and $f \simeq 100$ GHz this gives a moderate value of the required electric field $E_0 \simeq 5$ V/cm. The efficiency of the predicted frequency multiplication effect can be increased further by using the resonance response of the system at the plasmon, the cyclotron, or the magneto-plasmon frequency.

To summarize, we have investigated the non-linear electrodynamic response of 2D electrons and holes in graphene. We have shown that irradiation of graphene by an electromagnetic wave with frequency Ω should lead to generation of higher harmonics with frequencies 3Ω, 5Ω, etc. The efficiency of the frequency up-conversion is rather high: the amplitudes of the higher-harmonics of the ac electric current fall down slowly (as $1/m$) with harmonics index m. The presented quasi-classical theory is valid at $\hbar\Omega \lesssim \max\{\epsilon_F, T\}$. This estimate shows that the effect works at frequencies up to 5–10 THz, which opens up exciting opportunities for building new graphene devices for terahertz and sub-terahertz electronics.

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