Comment on “Graphene—A rather ordinary nonlinear optical material” [Appl. Phys. Lett. 104, 161116 (2014)]

S. A. Mikhailov
Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany
(Dated: April 26, 2018)

In 2007 it was predicted \(^\dagger\) that, due to the linear energy dispersion of quasi-particles in graphene, this material should have a strongly nonlinear electrodynamic response. This prediction stimulated a number of theoretical and experimental studies in which harmonics generation, four-wave mixing and other nonlinear phenomena have been observed. However, in April 2014 Khurgin published a paper \(^\ddagger\) entitled “Graphene—A rather ordinary nonlinear optical material”. In that paper the author performed a general qualitative analysis of the nonlinear properties of graphene, made order-of-magnitude estimates of nonlinear graphene parameters and came to a conclusion that practical nonlinear optical devices based on graphene will have no particular advantage over other materials. Therefore, a question arises whether the parameter \(\sigma^{(3)}/\sigma^{(1)}\) should be about \(\pi\), he estimated the factor \(\zeta\) as

\[
\zeta \equiv \frac{\sigma^{(3)} E^2}{\text{Re} \sigma^{(1)}} \approx \frac{1}{3} \quad \text{in Ref. } \ddagger \text{.}
\]

Here \(\sigma^{(1)}\) and \(\sigma^{(3)}\) are the first- and third-order conductivities, \(E_i = h\omega_i/\epsilon v_F\), \(\omega\) and \(E\) are the frequency and the electric field of the wave, and \(v_F \approx 10^6 \text{ cm/s}\) is the Fermi velocity in graphene; the estimate \(\ddagger\) was done at the telecommunication wavelength 1.55 \(\mu\)m where \(E_i \approx 10^7 V/cm\). Further the author writes “The nonlinear index for the interband transitions can become very large due to the resonant enhancement, but so does the absorption coefficient” and concludes that graphene is a quite ordinary nonlinear material at optical and near-infrared frequencies since the electric field needed for observation of essential nonlinear effects (~ \(10^7 V/cm\)) is very large.

Let us verify the validity of this conclusion. The third-order nonlinear properties of graphene are characterized by the fourth order tensor \(\sigma^{(3)}_{\alpha\beta\gamma\delta}(\omega_1,\omega_2,\omega_3)\) which depends on three input frequencies. At optical wavelengths, when all input frequencies \(h\omega_{1,2,3}\) exceed the double Fermi energy \(2E_F\) and \(\sigma^{(1)} \approx e^2/4\hbar\), the ratio \(\sigma^{(3)}/\sigma^{(1)}\) reads \(\ddagger\ddagger\):

\[
\frac{\sigma^{(3)}_{\alpha\beta\gamma\delta}(\omega_1,\omega_2,\omega_3)}{\sigma^{(1)}} = \frac{e^2v_F^2}{\hbar^2} \frac{1}{(\omega_1 + \omega_2 + i\gamma)(\omega_2 + \omega_3 + i\gamma)(\omega_3 + \omega_1 + i\gamma)(\omega_1 + \omega_2 + \omega_3 + i\gamma)^2}.
\]

A relevant quantity is \(\sigma^{(3)_{\alpha\beta\gamma\delta}}(\omega,\omega,\omega,\omega)\), with \(\omega_1 = \omega_2 = -\omega_3 = \omega\). In this case we get at \(\omega \gg \gamma\)

\[
\zeta_-(\omega) = \frac{\sigma^{(3)}_{\alpha\beta\gamma\delta}(\omega,\omega,\omega)}{\sigma^{(1)}} = \frac{1}{2} \frac{\omega^2}{\gamma^2}.
\]

At optical frequencies \(h\omega \approx 1 eV\) while the inter-band relaxation rate lies in the meV range \(\ddagger\ddagger\). The required electric field is then about \(\text{three orders of magnitude smaller}\) than the estimate \(\sim 10^7 V/cm\) obtained in \(\ddagger\ddagger\).

The statement that the nonlinear parameters of graphene could be substantially increased near inter-
the electron density \( n \) at different temperatures. Here \( E \) the parameters \( \alpha \) and \( \beta \) are similar to the conductivity \( \sigma \).

It was shown (see, e.g., a detailed discussion in Ref. 4) that the third conductivity \( \sigma_3 \) has a step-like behavior in the real part and a weak logarithmic resonance in the imaginary part. Figure 1 illustrates the resonant features of the parameters \( \zeta_\pm(\omega) \) in a broader range of frequencies from microwaves up to near-IR. One sees that at frequencies below \( \approx 100 \) THz the parameter \( \zeta_+(\omega) \) exceeds the estimate \( 2 \) by almost (more than) two orders of magnitude at room (cryogenic) temperatures, Fig. 1(a). The factor \( \zeta_-(\omega) \) exceeds the estimate \( 2 \) at all frequencies above few tens of THz by many orders of magnitude, Fig. 1(b).

In the second part of Ref. 2 the author discusses the low-frequency regime \( \hbar \omega \lesssim 2E_F \), where the nonlinear response is determined by the intra-band contributions to the conductivity. He agrees that at low doping densities the graphene response is highly nonlinear indeed, but remarks that at low densities the overall conductivity is small. The author concludes, in particular, that for operation around 30 THz the nonlinear graphene parameters are though respectable but not superior.

That graphene nonlinearities should be especially strong at low electron densities was emphasized already in the first publication. It was shown there that at low frequencies (\( \hbar \omega \lesssim 2E_F \)) the characteristic electric field which determines when the nonlinear effects in graphene become essential \( (E \gtrsim E_0) \) is given by

\[
E_0 = \frac{\hbar \omega k_F}{e} = \frac{\hbar \omega \sqrt{\pi n_s}}{e},
\]

where \( k_F \) is the Fermi wave-vector. As seen from \( 2 \) the in-band nonlinearity in graphene will be especially strong at low frequencies and low densities (say, at \( f \approx 1 \) THz and \( n_s \approx 10^{11} \) cm\(^{-2} \) rather than at \( f \approx 30 \) THz and \( n_s \approx 10^{12} - 10^{13} \) cm\(^{-2} \) as it was assumed in\(^2\)). If, for example, \( f = 1 \) THz and \( n_s = 10^{11} \) cm\(^{-2} \), the typical nonlinear electric field \( 4 \) is only 2.3 kV/cm which is three-four orders of magnitude smaller than in other materials. How large is then the nonlinear current, for example, the \( n \)-th harmonic current \( j_{n\omega} \), if the fundamental harmonic field exceeds a few kV/cm? According to\( 4 \), \( j_{n\omega} \approx 4e n_s v_F n \pi \) which gives (at 1 THz and \( n_s \approx 10^{11} \) cm\(^{-2} \)) huge for a single atomic layer values of \( j_{3\omega} \approx 0.68 \) A/cm, \( j_{5\omega} \approx 0.41 \) A/cm, etc. At higher frequencies, e.g. at 30 THz as discussed in\(^2\), one does not need to restrict himself by the intra-band contribution only. Choosing the Fermi energy so that \( \hbar \omega \) at 30 THz corresponds to \( 2E_F \) one gets \( |\zeta_-(\omega)| \approx 2000 \). This is achieved at \( E_F \approx 60 \) meV and \( n_s \approx 2.8 \times 10^{11} \) cm\(^{-2} \) which can be easily realized in graphene.

In summary, we have confirmed the statement of the original publication\(^1\) that nonlinear graphene parameters are orders of magnitude larger than in many other nonlinear materials and that nonlinear properties of graphene can be used in and are tunable across a very broad frequency range. The physical reasons for this are the linear energy dispersion of graphene electrons, which works at low — microwave, terahertz — frequencies, and the presence of inter-band resonances relevant at high — mid- and near-infrared, optical — frequencies. Both these features substantially reduce the electric fields needed for observation of nonlinear phenomena in graphene. We thus conclude, as opposed to Ref. 2, that the nonlinear graphene optics and electrodynamics is a promising and encouraging field of research.

The work has received funding from the European Unions Horizon 2020 research and innovation programme GrapheneCore1 under Grant Agreement No. 696656.
Email: sergey.mikhailov@physik.uni-augsburg.de

1 S. A. Mikhailov, Europhys. Lett. 79, 27002 (2007).
2 J. B. Khurgin, Appl. Phys. Lett. 104, 161116 (2014).
3 J. L. Cheng, N. Vermeulen, and J. E. Sipe, Phys. Rev. B 91, 235320 (2015), Erratum: Phys. Rev. B 93, 039904(E) (2016).
4 S. A. Mikhailov, Phys. Rev. B 93, 085403 (2016).
5 K. Alexander, N. A. Savostianova, S. A. Mikhailov, B. Kuyken, and D. Van Thourhout, ACS Photonics 4, 3039 (2017).
6 The second part of Ref. 2 contains some mistakes. The function $F_{\sigma 1}(x)$ cannot well approximate the function $F_{\sigma}(x)$ defined in Eq. (1) of Ref. 2 since at large $x \gg 1$ $F_{\sigma}(x)$ behaves as $1/x$ while $F_{\sigma 1}(x)$ as $4/x^2$. As a result, the formula (3) in Ref. 2 is incorrect.