Ultramicroscopy 184 (2018) 134–142

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Analytical modeling of electron energy loss spectroscopy of graphene: *Ab initio* study versus extended hydrodynamic model

Tijana Djordjević[a], Ivan Radović[a,*], Vito Despoja[b], Keenan Lyon[c], Duško Borka[a], Zoran L. Mišković[c,d]

[a] Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade 11001, Serbia
[b] Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, Zagreb 10000, Croatia
[c] Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
[d] Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

ARTICLE INFO

Article history:
Received 24 May 2017
Revised 12 August 2017
Accepted 29 August 2017
Available online 4 September 2017

Keywords:
Graphene
Ab initio
Hydrodynamic model
(S)TEM
EELS

ABSTRACT

We present an analytical modeling of the electron energy loss (EEL) spectroscopy data for free-standing graphene obtained by scanning transmission electron microscope. The probability density for energy loss of fast electrons traversing graphene under normal incidence is evaluated using an optical approximation based on the conductivity of graphene given in the local, i.e., frequency-dependent form derived by both a two-dimensional, two-fluid extended hydrodynamic (eHD) model and an *ab initio* method. We compare the results for the real and imaginary parts of the optical conductivity in graphene obtained by these two methods. The calculated probability density is directly compared with the EEL spectra from three independent experiments and we find very good agreement, especially in the case of the eHD model. Furthermore, we point out that the subtraction of the zero-loss peak from the experimental EEL spectra has a strong influence on the analytical model for the EEL spectroscopy data.

1. Introduction

With its unique electrical and optical properties (relatively low loss, high confinement, mechanical flexibility, and good tunability) graphene is an ideal material for plasmonic applications covering a wide frequency range from terahertz up to infrared, even stretching into the visible regime [1–4]. Electron energy loss spectroscopy (EELS) is a commonly used experimental technique for investigating electronic and plasmonic properties of materials, including graphene sheets [1]. High-energy single-particle inter-band excitations in graphene, which are often misnomered as π and $\pi+\sigma$ plasmons [5], have been studied recently by EELS experiments using high-energy electron beams (~100 keV) in scanning transmission electron microscope (STEM) on samples consisting of free-standing, single-layer graphene (SLG) [5–12], and multi-layer graphene (MLG) [8–12].

Theoretical modeling of the EELS data of SLG and MLG is an active field of research [13–19]. In our previous publication [20], we treated the MLG as layered electron gas with in-plane polarizability modeled by a two-dimensional (2D), two-fluid hydrodynamic (HD) model [21] for the inter-band transitions of π and σ electrons of SLG, yielding good agreement with the experimental EEL spectra [11] for $N<10$ graphene layers in STEM. We have also used the same version of the HD model for graphene's π and σ electrons in conjunction with an empirical Drude-Lorentz model for metal substrate to reproduce the momentum-resolved experimental EELS data for low-energy electron reflection (~10 eV) from monolayer graphene supported by Pt(111), Ru(0001), and Ni(111) substrates [19], as well as for high-quality graphene grown on peeled-off epitaxial Cu(111) foils [22].

It should be mentioned that, while the agreement of the HD model with the experimental EEL spectra for MLG from Ref. [11] covered the regions around the principal π and $\pi+\sigma$ peaks, there was no experimental data for energy losses below $\approx$3 eV, which is a consequence of the subtraction of the zero-loss peak (ZLP). At the same time, the HD model does not incorporate the Dirac physics of low-energy excitations in graphene [20]. However, in the meantime, several EELS experiments were performed with high-energy electron beams in STEM, showing intriguing increase in spectral intensity as the energy loss decreases below $\approx$3 eV, even after the ZLP subtraction [5,7,12]. In that respect, we pose a question whether the low-energy, inter-band excitations of π electrons in intrinsic graphene play any detectable role in the low-loss range of EELS, and if so, whether the new generation of monochromators can open up possibility to explore the Dirac physics of

* Corresponding author.
E-mail address: iradovic@vin.bg.ac.rs (I. Radović).

http://dx.doi.org/10.1016/j.ultramic.2017.08.014
0304-3991/

graphene in STEM. In order to address this question, we attempt to reproduce the STEM-EELS data from those experiments [5,7,12] by formulating an extended HD (eHD) model, which includes a Dirac correction. This correction treats the low-energy contribution of graphene's π electron inter-band transitions in a manner consistent with the Dirac-cone approximation for graphene's π electron bands near the K point in the Brillouin zone (BZ).

On the other hand, Despoja et al. have used an *ab initio* method to calculate the energy-loss rate of a point blinking charge in the vicinity of a graphene monolayer [23] and have obtained values for the energies of π and $\pi+\sigma$ peaks in the EELS spectra, which are in good agreement with the reported experimental values [11]. In addition, they have calculated the so-called loss function, $\mathrm{Im}[-1/\varepsilon(q,\omega)]$, where $\varepsilon(q,\omega)$ is the dielectric function of SLG obtained by *ab initio* methods [24], and have obtained a very good agreement with the experimental STEM-EELS data for SLG [11]. Moreover, those authors were able to implement their *ab initio* method in the optical, or the long wavelength limit ($q\to 0$), and hence compute a universal, frequency dependent 2D conductivity of SLG, $\sigma(\omega)$, in a broad range of energies of interest for EELS in STEM [25]. At the same time, it was observed in Ref. [5] that using a response function of graphene in the optical limit represents an excellent approximation for analytical modeling of the EELS data with the electron beam under normal incidence and for small collection angles. Taking advantage of that situation, we propose here an analytical expression for the optical conductivity $\sigma(\omega)$ of SLG within the eHD model, containing several free parameters which are fixed via direct comparison with the optical conductivity obtained by the *ab initio* method.

Moreover, taking further advantage of working in the limit of optical response of SLG, we derive an analytical expression for the probability density for losing energy ω, $P(\omega)$, of fast electrons traversing graphene under normal incidence, which takes frequency dependent conductivity $\sigma(\omega)$ as input. The resulting formula may be readily applied to model the EELS of any isotropic 2D material, which can be described by a scalar conductivity given in local form. Hence, we use both the eHD and *ab initio* results for $\sigma(\omega)$ of SLG to obtain probability densities $P(\omega)$ which are then directly compared with the experimental EELS data from three independent experiments.

Finally, using the eHD model with and without the Dirac correction, we explore the possible role of Dirac physics in the experimental STEM-EELS setup and its effects on the ZLP subtraction from those spectra.

2. Theoretical methods

In a typical (S)TEM-EELS experiment operating at the voltage on the order of several tens of kV (for example, 40 kV in Ref. [7], 60 kV in Ref. [5], and 100 kV in Ref. [11]) the momentum transfer of the incident electron is close to zero, so we shall use a straight-line trajectory while neglecting relativistic effects [20,26]. We use a Cartesian coordinate system with $\vec{r}=\{\vec{R},z\}$ and assume that SLG occupies the plane $z=0$, where $\vec{R}=\{x,y\}$ is the in-plane position and z the distance from it. Following Ref. [20], one may express the probability density, $P(\omega)$, for energy loss of an incident electron traversing the SLG, which, including the nonlocal effects of the dynamic response of graphene, can be expressed as (using Gaussian electrostatic units and denoting the charge of a proton by $e>0$)

$$P(\omega)=\frac{e^2}{2\pi^2\hbar^2}\int\frac{K^2(q,\omega-\vec{q}\cdot\vec{v}_{||})}{q}\mathrm{Im}\left[-\frac{1}{\varepsilon(\vec{q},\omega)}\right]d^2\vec{q}, \quad (1)$$

where

$$K(q,\omega-\vec{q}\cdot\vec{v}_{||})=\frac{2qv_\perp}{(\omega-\vec{q}\cdot\vec{v}_{||})^2+(qv_\perp)^2}, \quad (2)$$

with $\vec{v}_{||}$ and $v_\perp$ being the velocity components of the incident electron parallel and perpendicular to the graphene plane, respectively, and

$$\varepsilon(\vec{q},\omega)=1+\frac{2\pi e^2}{q}\chi(\vec{q},\omega), \quad (3)$$

being the 2D dielectric function of SLG with $\chi(\vec{q},\omega)$ being its polarizability, which describes the linear response of independent (non-interacting) electrons.

The probability density $P(\omega)$ will be directly compared with the experimental EEL spectra of SLG which was taken under normal electron incidence using circular aperture that collects all scattered electrons [5,11]. Setting $\vec{v}_{||}=\vec{0}$ in Eqs. (1) and (2) and invoking the near-isotropy of graphene's polarizability, $\chi(\vec{q},\omega)=\chi(q,\omega)$, one obtains

$$P(\omega)=\frac{4e^2}{\pi\hbar^2v_\perp^2}\int_0^{q_c}\frac{q^2}{\left[q^2+\left(\frac{\omega}{v_\perp}\right)^2\right]^2}\mathrm{Im}\left[-\frac{1}{1+\frac{2\pi e^2}{q}\chi(q,\omega)}\right]dq, \quad (4)$$

where $q_c=k_0\beta$ is the maximum collected in-plane scattering momentum of the incident electron with k_0 being its total momentum and β the scattering semi-angle.

The polarizability $\chi(q,\omega)$ may be approximately expressed in terms of the conductivity of graphene $\sigma(\omega)$ in the long wavelength limit ($q\to 0$) as

$$\chi(q,\omega)\approx i\frac{q^2}{e^2\omega}\sigma(\omega), \quad (5)$$

which, when substituted in Eq. (4), enables the integration over q to be completed analytically, giving

$$P(\omega)=-\frac{4e^2}{\pi\hbar^2}\mathrm{Im}\left\{\frac{B}{\omega v_\perp}\left[F\left(\frac{q_cv_\perp}{\omega}\right)-F(0)\right]\right\}, \quad (6)$$

where $F(x)$ is given by

$$F(x)=\int\frac{x^2}{(x^2+1)^2(B+x)}dx=-\frac{xB+1}{2(x^2+1)(B^2+1)}+\frac{B(B^2-1)\arctan(x)}{2(B^2+1)^2}+\frac{B^2}{(B^2+1)^2}\left[\ln(B+x)-\frac{1}{2}\ln(x^2+1)\right], \quad (7)$$

with

$$B\equiv -i\frac{v_\perp}{2\pi\sigma(\omega)}. \quad (8)$$

It should be noted that in some experimental situations [5,11] the maximum in-plane momentum q_c is large enough, so that no difference occurs in the final results for $P(\omega)$ if the upper limit is extended to $q_c\to\infty$ because the kinematic factor $K^2(q,\omega)$ in Eq. (1) is strongly peaked at $q=\omega/v_\perp << q_c$ for the relevant frequency range (cf. Eq. (2)). Thus, to a very good approximation, one may then use the limit $q_cv_\perp/\omega >> 1$, giving

$$F(\infty)=\frac{\pi}{4}\frac{B(B^2-1)}{(B^2+1)^2}, \quad (9)$$

which with

$$F(0)=\frac{2B^2\ln(B)-B^2-1}{2(B^2+1)^2} \quad (10)$$