

## An Anisotropic Approach for Simulating Electron Transport in Layered Materials: Computational and Experimental Study of Highly Oriented Pyrolytic Graphite

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*J. Phys. Chem. C*, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.8b02256 • Publication Date (Web): 16 Apr 2018

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## Abstract

In this work, we propose a theoretical and computational model for taking into account the anisotropic structure of Highly Oriented Pyrolytic Graphite (HOPG) in the Monte Carlo simulations of charge transport. In particular, the dielectric characteristics, such as the inelastic mean free path and energy losses, are treated by linearly combining the contributions to these observables along the two main orthogonal directions identifying the layered crystalline structure of HOPG (along the layer plane and perpendicular to it). Energy losses are evaluated from *ab initio* calculations of the dielectric function of the system along these two perpendicular directions. Monte Carlo simulated spectra, obtained with our anisotropic approach, are compared with acquired experimental data of Reflection Electron Energy Loss and Secondary Electron spectra, showing a good agreement. These findings validate the idea of the importance of considering properly-weighted inter-planar and intra-planar interactions in the simulation of electron transport in layered materials.

## Introduction

Carbon-based materials have recently attracted significant attention due to the discovery of new exciting science, particularly in connection with the unique band structure of graphene. Within this 2D material, in which the planar topology is realized by a  $sp^2$ -net of carbon atoms, electrons behave like relativistic fermions offering the potential for high speed nanoscale electronics and for replacing silicon in light-weight and wearable devices. Other carbon allotropes, obtained for example by rolling up graphene in carbon nanotubes, display further interesting properties, as they can be produced with both semiconducting and metallic character depending on the twist and on the diameter of the tube.<sup>1,2</sup> Nevertheless, these materials are still difficult to be synthesized in a cost-effective, scalable way.

At variance with other allotropes of carbon, graphite can be naturally found (the others two being amorphous carbon and diamond). Thus, it is worthy to explore its properties,

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3 particularly with respect to its electronic characteristics for applications in opto-electronic  
4 devices and imaging. Graphite represents a 3D stacking of graphene sheets, and thus dis-  
5 play an uniaxial layered structure which retains some characteristics of graphene, while its  
6 thermal, acoustic and electronic properties are highly anisotropic. Most notably, the large  
7 anisotropy of the electric conductivity means that along the planes graphite shows an higher  
8 conductivity than in the direction normal to the surface<sup>3</sup>.

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10 In this work we present Monte Carlo (MC) simulations of Reflection Electron Energy Loss  
11 (REEL) and Secondary Electron (SE) spectra of Highly Oriented Pyrolytic Graphite (HOPG),  
12 taking into account the target anisotropic structure. Simulated spectra are compared with  
13 experimental data recorded in our laboratories. In this model, elastic scattering events be-  
14 tween electrons and target atoms are treated via the Mott theory<sup>4</sup>, which is based on the  
15 solution of the Dirac equation in a central field. At variance, inelastic collisions between the  
16 primary electron beam and the electron cloud of the target can result in the excitation of  
17 bulk and surface plasma oscillations. In this regard, an accurate description of the electron  
18 energy loss is provided by the dielectric theory developed by Ritchie<sup>5</sup>. Within this approach,  
19 the key quantity for the calculation of the inelastic cross section is the Energy Loss Function  
20 (ELF), defined as the imaginary part of the inverse of the dielectric function  $\epsilon(\vec{q}, W)$ , where  
21  $\vec{q}$  is the transferred momentum owing to the inelastic interactions and  $W$  is the energy loss.  
22 To take into account graphite anisotropy, we assess from *ab initio* time-dependent density  
23 functional simulations the dielectric function optical limit ( $\epsilon_{\vec{q} \rightarrow 0}$ ) along two orthogonal di-  
24 rections: along the direction normal to the layer (identified by the vector  $\vec{c}$ ), which accounts  
25 for inter-planar interactions, and along that one perpendicular to  $\vec{c}$ , which describes intra-  
26 planar excitations (in-plane direction). Finally, the ELFs, obtained by combining these two  
27 dielectric functions, were fitted in the optical limit by using Drude–Lorentz functions, and  
28 extended to finite momenta by a dispersion law obtained within the Random Phase Approx-  
29 imation (RPA)<sup>6</sup>. In this way, the energy losses in both planar and inter-planar directions  
30 were taken into account appropriately in our Monte Carlo simulations.  
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3 In the following sections the Monte Carlo model as well as the experimental procedures will  
4 be described in details. Then the comparison between experimental and simulated spectra  
5 will be presented.  
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## 10 11 **Experimental Details**

### 12 13 14 **Reflection Electron Energy Loss Spectra Acquisition**

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17 The sample of HOPG was initially cleaved ex-situ, and then was cleaned by annealing at  
18 600 °C for 10 min in ultra-high vacuum. The REEL measurements were realized at a base  
19 pressure of  $\approx 2 \times 10^{-2}$  mbar in a PHI 545 system. The experimental apparatus is composed  
20 by a coaxial electron gun, a non-monochromatic  $\text{MgK}\alpha$  ( $h\nu = 1253.6$  eV) X-ray source, a  
21 He discharge lamp and double-pass cylindrical mirror analyser (CMA). In CMA, the angle  
22 between primary electron beam and the surface normal is maintained constant, while emitted  
23 electrons cross the surface in different directions that are described by the angle between  
24 the surface normal and the CMA axis ( $30^\circ$ ), the entrance angle to the analyser ( $42^\circ \pm 6^\circ$ )  
25 ) and the azimuth angle in a plane normal to the CMA axis. The energy resolution was  
26 maintained constant at 0.6 eV, as measured on a Pd Fermi edge. The zero-loss peak has a  
27 measured full width half maximum of 0.9 eV. The energy of the impinging electron beam  
28 spans the range from 250 eV to 2000 eV. The acquired spectra are corrected for the energy  
29 dependence ( $E^{-0.9}$ ) accordingly to the analyser transmission function.  
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### 45 46 **Secondary Electron Spectrum Acquisition**

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48 SE spectrum acquisition was performed with a FEI Helios NanoLab G3 UC scanning electron  
49 microscope (SEM). HOPG with a mosaic spread of  $3.55^\circ \pm 1.5^\circ$  (purchased from Agar  
50 scientific) was mounted on an aluminium pin-stub using silver paint. Prior to specimen  
51 insertion into the SEM, the HOPG surface was mechanically exfoliated. The maximum time  
52 between exfoliation, insertion into the SEM vacuum chamber and pump down to vacuum  
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3 was less than 3 minutes. For imaging and spectra collection, the vacuum pressure at room  
4 temperature was  $3 \times 10^{-6}$  mbar and the working distance was kept to 4 mm. The design of the  
5 in-lens detector of this SEM allows the collection of different SE energy ranges by changing  
6 a mirror electrode voltage (M parameter). Images were collected at different M settings  
7 ranging from minimum electron energy of -0.7 eV to a maximum of 12.7 eV. SE spectra were  
8 collated by differentiating the mean intensity of each image from each individual M step. SE  
9 energy calibration method for this system can be found in Young et al.<sup>7</sup> and the supporting  
10 information of Wan et al.<sup>8</sup>, whilst the absolute energy value was checked by fine structures  
11 reported experimentally in literature (3, 4 and 7.5 eV<sup>9</sup>) for HOPG and fine structure for  
12 diamond (6 eV<sup>10</sup>). Detection artifacts within a certain M range were identified by evaluating  
13 the average intensity of a reference gold sample with the smallest possible filter parameter  
14 step difference (0.1 V). The artefacts manifested as an increment in M without an associated  
15 signal change, signifying a discrepancy between the stated and actual M. A lookup table of  
16 corrected M was created, excluding the artefacts and re-scaling the remaining M to the initial  
17 filter parameter collection range. The differentiation of the S-curve to obtain the spectrum  
18 was performed using the corrected SE energy values associated with the respective M values.  
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## 37 Computational Details

### 40 Elastic Scattering

41 Elastic scattering between the impinging electrons and the atoms of the target is described by  
42 the Mott theory (see, for example,<sup>11-15</sup>). The atomic potential was obtained self-consistently  
43 by solving the Dirac-Kohn-Sham equations for the carbon atom within the local-spin-density  
44 approximation (LSDA) as implemented in the ELK software program<sup>16</sup>. The elastic scat-  
45 tering cross-section is calculated as reported in Ref.<sup>17</sup>.

46 For  $T = 10$  eV we find a total elastic scattering cross-section  $\sigma_{\text{el}} = 28.3 \text{ \AA}^2$  and an elastic  
47 mean free path  $\lambda_{\text{el}} = 0.31 \text{ \AA}$ . This value of  $\lambda_{\text{el}}$  is one order of magnitude lower than the  
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lattice parameters of graphite ( $\vec{a} = 2.46 \text{ \AA}$ ,  $\vec{c} = 6.71 \text{ \AA}$ ) and is thus unphysical. Therefore, we introduce a correction to the Mott cross-section at low energy.<sup>18</sup> Ganachaud and Mokrani<sup>19</sup> proposed to multiply the total elastic scattering cross-section  $\sigma_{\text{el}}$  by a cut-off function in order to diminish  $\sigma_{\text{el}}$  at low energy. Similarly to this model, the total elastic scattering cross-section can be obtained by multiplying the cross section calculated using the partial-wave expansion method by the following factor:

$$R(T) = \tanh(\alpha T^2) \quad (1)$$

where  $\alpha$  is a parameter to be determined. It is worth noting that in the previous function, the  $\alpha$  parameter is different from the  $\alpha_C$  parameter of the Ganachaud and Mokrani cut off function. Indeed, the latter includes also the material energy band gap. By choosing  $\alpha = 0.003 \text{ 1/eV}^2$  the value of the elastic mean free path for  $T = 10 \text{ eV}$  is  $\lambda_{\text{el}} = 1.15 \text{ \AA}$ . Fig. 1 shows the behavior of  $\sigma_{\text{el}}$  (left panel) and  $\lambda_{\text{el}}$  (right panel) obtained with  $\alpha = 0.003 \text{ eV}^{-2}$ , along with those calculated by using the bare Mott theory. By introducing this factor,

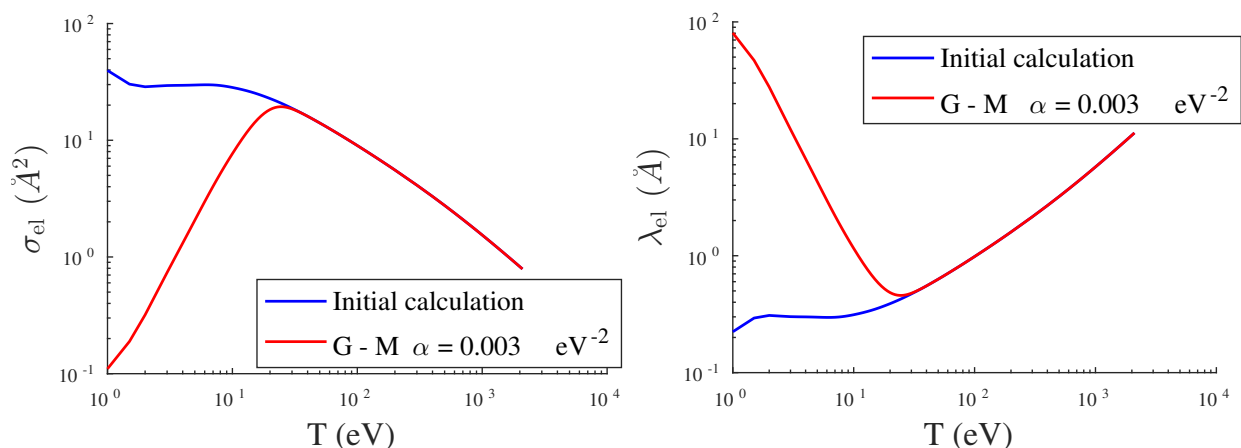


Figure 1: Total elastic scattering cross-section  $\sigma_{\text{el}}$  (left panel) and elastic mean free path  $\lambda_{\text{el}}$  (right panel) calculated from the bare Mott theory (blue line) and by using the correction proposed by Ganachaud and Mokrani ( $\alpha = 0.003 \text{ 1/eV}^2$ ) (red line).

one obtains a behaviour of the elastic scattering cross-section consistently decreasing at low energy.

Moreover, we find out that the use of a cut-off function is necessary to obtain a good agreement between calculated and experimental SE spectra.

## Inelastic Scattering

The inelastic scattering between the impinging electrons and the electron clouds of the target atoms was dealt with the Ritchie theory<sup>5</sup>.

Within this approach, the total inelastic cross-section can be computed by assessing the inelastic mean free path  $\lambda_{\text{inel}}$  (IMFP). The latter can be obtained by integrating over the energy loss interval the differential inverse inelastic mean free path (DIIMFP):

$$\lambda_{\text{inel}}^{-1} = \int_0^{T/2} \frac{d\lambda_{\text{inel}}^{-1}}{dW} dW \quad (2)$$

where  $T$  is the primary beam kinetic energy and the DIIMFP is defined as:

$$\frac{d\lambda_{\text{inel}}^{-1}}{dW} = \frac{1}{\pi T a_0} \int_{q_-}^{q_+} \frac{dq}{q} \text{Im} \left[ -\frac{1}{\epsilon(\vec{q}, W)} \right] \quad (3)$$

where  $a_0$  is the Bohr radius. The limits of integration of the integral in Eq. (3) are set to  $q_{\pm} = \sqrt{2mT} \pm \sqrt{2m(T - W)}$  for momentum conservation<sup>11</sup>. The integrand in Eq. (3) is the so-called ELF.

According to Eq. (3), to model the inelastic collisions one needs to compute the dielectric function of the target material as a function of the momentum  $\vec{q}$  and of the energy transferred during the inelastic collision  $W$ . ELFs were calculated in the optical limit ( $\vec{q} \rightarrow 0$ ) from *ab initio* simulations using the ELK code<sup>16</sup> within the framework of Linear Response Time Dependent Density Functional Theory (LR-TDDFT). In these calculations we used a  $k$ -point sampling of  $20 \times 20 \times 20$  mesh points, a cut-off for augmented plane waves equal to 400 eV, and a Fermi-smearing of 0.2 eV.

Considering the anisotropic structure of HOPG, two possible different orientations for energy losses were taken into account: on the one hand, we considered the transferred momentum



$\vec{q}$  parallel to the vector normal to the graphite plane (identified by the vector  $\vec{c}$ ), and on the other hand  $\vec{q}$  perpendicular to  $\vec{c}$ . Dielectric functions and derived observables, such as inelastic mean free paths, are reported for these two cases in the following discussion respectively as  $\epsilon_{\parallel}(q, W)$  and  $\epsilon_{\perp}(q, W)$ , as well as the same notation is applied to the inelastic mean free paths  $\lambda_{\parallel}$  and  $\lambda_{\perp}$ . Optical ELF's were then fitted by Drude–Lorentz (D-L) functions as follows:

$$ELF = \sum_n \frac{A_n \Gamma_n W}{(E_n^2(q) - W^2)^2 + (\Gamma_n W)^2} \quad (4)$$

where  $A_n$  is the excitation strength of the  $n$ -th oscillator,  $\Gamma_n$  the damping constant, and  $E_n$  the plasmon excitation energy. In Fig. 2 *ab initio* data and final fit functions are shown, while in Tabs. 1 and 2 the fitting parameters are reported. In the fitting procedure the number of oscillators was chosen to reproduce the *ab initio* spectra. Moreover, the choice of these optimal parameters leads to fulfilling the f-sum rule.

Table 1: D–L parameters ( $\vec{q} \parallel \vec{c}$  direction)

$n$	$A_n$ (eV <sup>2</sup> )	$\Gamma_n$ (eV)	$E_n$ (eV)
1	0.15	1.75	0.80
2	0.62	1.76	4.06
3	13.26	4.22	15.57
4	51.80	1.90	18.23
5	25.52	6.23	20.73
6	452.31	20.02	37.93
7	112.91	19.84	48.25

Table 2: D–L parameters ( $\vec{q} \perp \vec{c}$  direction)

$n$	$A_n$ (eV <sup>2</sup> )	$\Gamma_n$ (eV)	$E_n$ (eV)
1	0.43	5.36	2.58
2	8.96	1.73	6.99
3	0.25	8.30	14.53
4	33.93	10.16	21.77
5	32.00	10.50	24.32
6	466.69	6.99	28.03
7	100.30	30.03	38.09

Finally, ELF fit functions are extended to finite values of  $\vec{q}$  by applying the quadratic

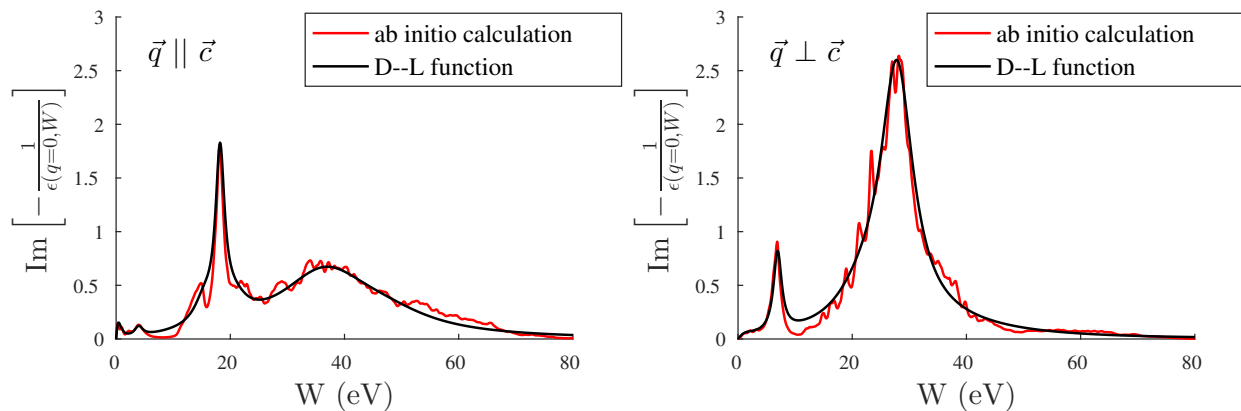


Figure 2: ELF functions along the two possible orthogonal directions of transferred momentum  $\vec{q}$ : *ab initio* calculations (red lines) are compared to the Drude–Lorentz best fits (black lines).

dispersion law obtained within the RPA<sup>6</sup>:

$$E_n(q \neq 0) = E_n(q = 0) + \frac{\hbar^2 q^2}{2m} \quad (5)$$

These data were used to compute the total inelastic scattering cross-section  $\sigma_{\text{inel}}$  and the IMFP  $\lambda_{\text{inel}}$  by Eq. (2) (see Fig. 3).

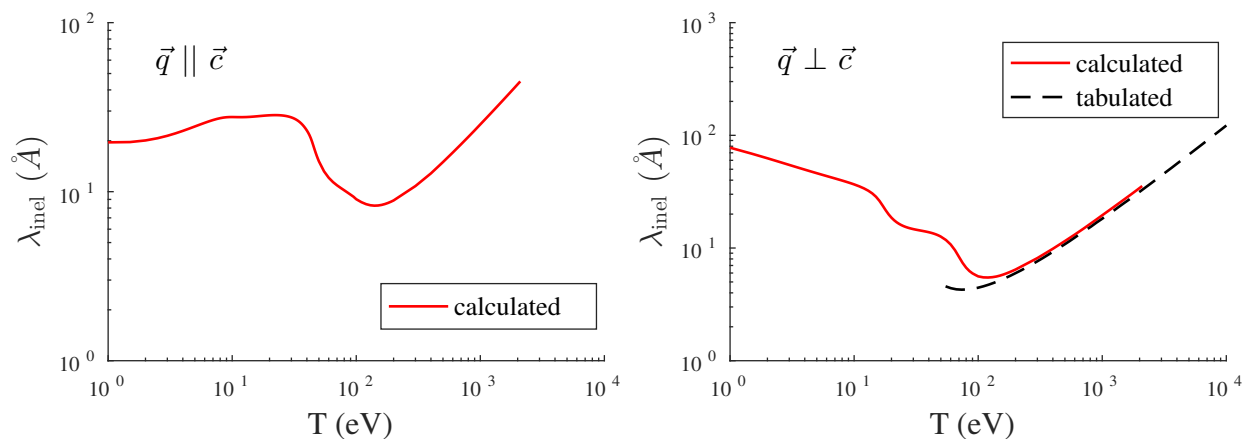


Figure 3: Inelastic mean free paths calculated along the two possible orthogonal directions of transferred momentum  $\vec{q}$ . In the case  $\vec{q} \perp \vec{c}$  the calculated values are compared with the data by Tanuma et al. (dashed lines)<sup>20</sup>.

To calculate the total IMFP by taking into account the anisotropic structure of graphite,  $\lambda_{\text{inel}}$  and  $W$  were determined by linearly combining at each inelastic interaction the corre-

sponding values along the two possible orthogonal directions of the transferred momentum  $\vec{q}$ , as follows:

$$\lambda_{\text{inel}} = f \cos^2 \theta \lambda_{\parallel} + [(1 - f) + f \sin^2 \theta] \lambda_{\perp} \quad (6)$$

$$W = f \cos^2 \theta W_{\parallel} + [(1 - f) + f \sin^2 \theta] W_{\perp} \quad (7)$$

where  $f$  is an *anisotropy parameter* in the range [0:1], and  $\theta$  is the angle between  $\vec{c}$  and  $\vec{q}$ . The  $f$  parameter has been introduced in this anisotropic model of the inelastic observables to favour the electron motion in the planar direction, since HOPG shows a higher conductivity along the plane ( $\vec{q} \perp \vec{c}$ ). The value of  $f$  is determined to obtain the best agreement between theoretical and experimental spectra.

## Monte Carlo Model

Monte Carlo simulations were performed in order to interpret REEL and SE spectra of HOPG acquired in-house. Details on our Monte Carlo approach can be found in Ref.<sup>21</sup>.

To carry out Monte Carlo calculations some input information about the target material, such as atomic and mass number, density, elastic and inelastic mean free paths and probability distributions of elastic and inelastic scattering, is required. In particular, the characteristic quantities of the target material are: the atomic number ( $Z = 6$ ), the atomic mass ( $A = 12.011 \text{ uma}$ )<sup>22</sup>, the density ( $d = 2.25 \text{ g/cm}^3$ )<sup>23</sup>, the electronic band gap  $E_g$  (0.0 eV), and the work function ( $WF = 4.6 \text{ eV}$ )<sup>24</sup>.

On the one hand, in the case of inelastic collisions the primary electrons lose their kinetic energy according to the cumulative probability distribution:

$$P_{\text{inel}}(T, W) = \lambda_{\text{inel}} \int_{E_g}^W \frac{d\lambda_{\text{inel}}^{-1}}{dW'} dW' \quad (8)$$

that depends on the initial kinetic energy  $T$  and on the energy loss  $W$ .

On the other hand, the change in the direction of the elastically scattered electrons can be

obtained by using the elastic cumulative probability:

$$P_{\text{el}}(T, \bar{\theta}) = \frac{2\pi}{\sigma_{\text{el}}} \int_0^{\bar{\theta}} \frac{d\sigma_{\text{el}}}{d\theta'} \sin \theta' d\theta' \quad (9)$$

that is determined for a fixed initial kinetic energy  $T$  by varying the scattering angle  $\theta$  in the range  $[0, \bar{\theta}]$ . In Eq. (9)  $\sigma_{\text{el}}$  is the total elastic scattering cross-section.

Elastic and inelastic scattering probability distributions lead respectively to the assessment of the scattering angle and of the energy loss. Probability distributions were calculated at specific energies of the electrons, and in Tab. 3 we report both the electron kinetic energy ranges and the relevant mesh intervals ( $\Delta E$ ) that we used in our MC simulations.

Table 3: Energy values at which scattering probabilities are calculated.

range	$\Delta E$
$0 < E \leq 10$ eV	$\Delta E = 0.5$ eV
$10 < E \leq 50$ eV	$\Delta E = 1.0$ eV
$50 < E \leq 100$ eV	$\Delta E = 5.0$ eV
$100 < E \leq 200$ eV	$\Delta E = 10.0$ eV
$E \geq 200$ eV	$\Delta E = 100.0$ eV

Depending on the kinetic energy of the electron undergoing the collision, we select a probability distribution. The scattering angle (elastic interaction) or the energy loss (inelastic interaction) are determined by generating a random number, uniformly distributed in the interval  $[0,1]$ . In fact, (see Eq.(9)) the value of the elastic scattering cumulative probability (or of the inelastic scattering cumulative probability, see Eq. (8) ) that equalizes this random number determines the scattering angle (or the energy loss). The total mean free path ( $\lambda$ ), which characterizes the electron path within the target material is defined as:

$$\frac{1}{\lambda} = \frac{1}{\lambda_{\text{el}}} + \frac{1}{\lambda_{\text{inel}}} \quad (10)$$

where  $\lambda_{\text{el}}$  is the elastic mean free path. The probabilities of the elastic and inelastic events

can be evaluated, for any fixed value of kinetic energy and angle, as:

$$p_{\text{el}} = \frac{\lambda}{\lambda_{\text{el}}} \quad p_{\text{inel}} = \frac{\lambda}{\lambda_{\text{inel}}} \quad (11)$$

The decision on the type of collision that the electrons undergo is made by generating another random number uniformly distributed in the interval  $[0,1]$ . Whether this number is lower than  $p_{\text{el}}$  the interaction will be elastic, otherwise it will be inelastic. In Fig. 4 we report the elastic and inelastic collision probabilities as a function of the relevant variables  $\theta$  and  $T$ .

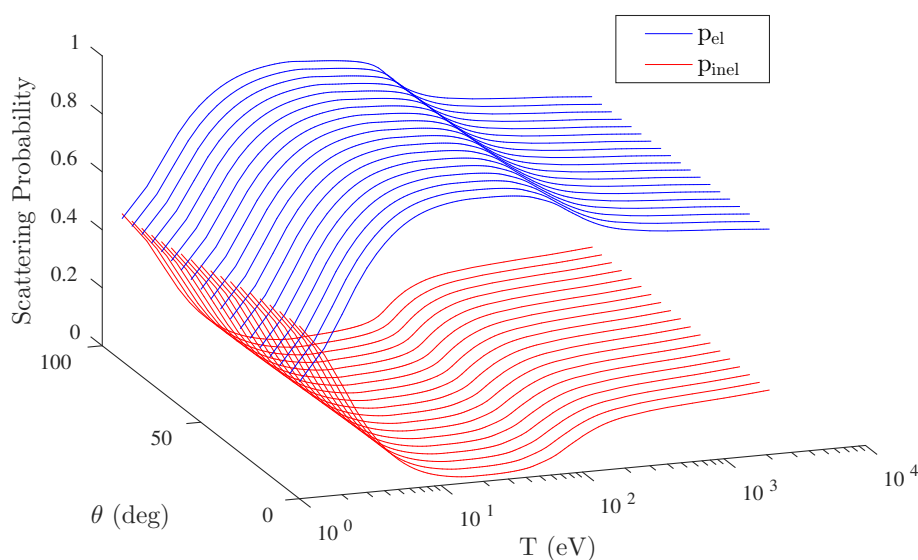


Figure 4: Collision probabilities as a function of the electron kinetic energy ( $T$ ) and of the angle ( $\theta$ ) between the transferred momentum  $\vec{q}$  and the vector  $\vec{c}$  normal to the surface.

## Results and Discussion

### REELS

Different simulations were carried out at several beam kinetic energies to simulate our recorded REEL spectra. In the Monte Carlo runs, the trajectories of  $N = 10^9$  primary electrons were followed in order to achieve a good statistics. The beam incidence angle was fixed at  $30^\circ$  with respect to the normal to the surface, according to our experimental

conditions. First, we investigated the dependence of the REEL spectra on the parameter  $f$  by spanning a range of possible values in Eqs. (6) and (7). Fig. 5 compares the REEL theoretical spectra (red lines), obtained for an initial kinetic energy of 1500 eV, at different values of  $f$  with our experimental data (black lines)<sup>21</sup>.

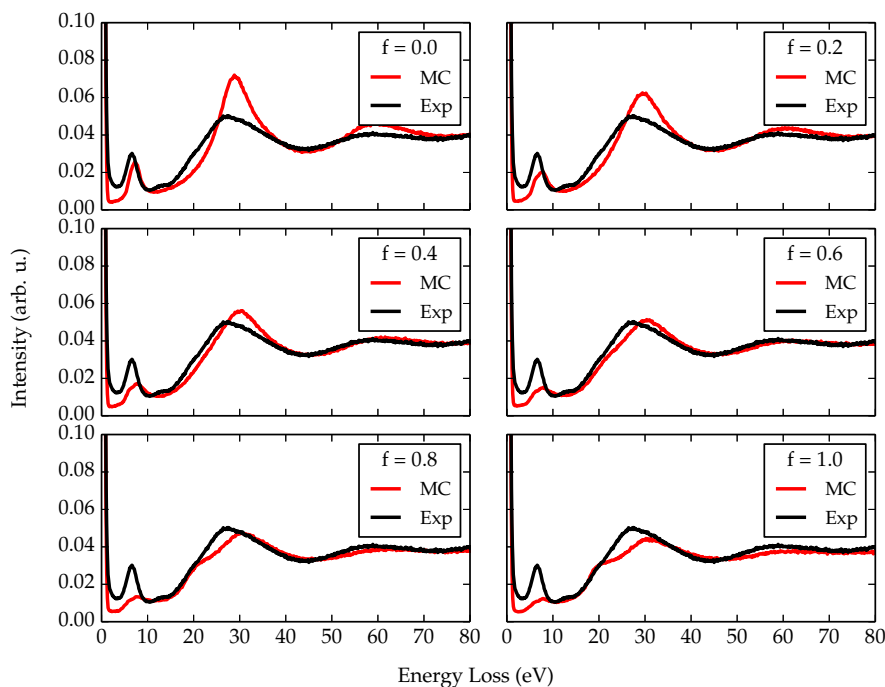


Figure 5: REELs of HOPG for different values of the  $f$  parameter (red lines). The kinetic energy of the primary beam is set to 1500 eV. MC calculations are compared with our experimental data (black lines)<sup>21</sup>. The spectra are normalized at a common area of the elastic peak.

The higher the value of  $f$ , the larger is the contribution of intra-planar excitations ( $\vec{q}||\vec{c}$ ) to inelastic interactions. This effect can be noticed in the spectra of Fig. 5 by the rise of a shoulder at an energy loss of 20 eV, which corresponds to an oscillation in the ELF along the  $\vec{q}||\vec{c}$  direction. The value of the anisotropy parameter that shows the best agreement between experimental and calculated REELS normalized at a common area of the elastic peak is  $f = 0.6$ . Indeed, by performing a chi-squared test in the energy loss range [-2:80] eV, the lowest value of the  $\chi^2$  can be obtained using  $f = 0.6$  (see table 4). Nevertheless, a value equal to 0.6 of this anisotropic parameter delivers the best agreement also in other

primary beam energy ranges. Thus, we set the anisotropy parameter to this value in all MC simulations. This means physically that by considering e.g. a scattering angle  $\theta = 0^\circ$  (that is,

Table 4:  $\chi^2$ -test carried out by considering the experimental and calculated data normalized at a common area of the elastic peak in the energy loss range [-2:80] eV for different values of the parameter  $f$ .

$f$	$\chi^2$
0.0	134
0.2	207
0.4	125
0.6	93
0.8	95
1.0	174

orthogonal to the graphite layers), the energy loss embeds 60% of collisions with a transferred momentum along the  $\vec{q}||\vec{c}$  direction, while 40% of the spectrum is made by collisions along the  $\vec{q}\perp\vec{c}$  (in-plane) direction (see Eqs. (6) and (7)). Of course, the directional change of the electrons inelastically scattered by the target nuclei is taken into account, for fixed  $f$ , by the scattering angle  $\theta$ , which is modified by the interactions at each MC step. This anisotropic model is consistent with the higher tendency of the electrons to move along the graphite planes rather than across the planes.

MC simulations were performed at several primary beam kinetic energies and compared with our experimental data (normalized at a common area of the elastic peak) in Fig. 6.

We notice that the agreement between calculated and experimental data is rather good and becomes progressively better for increasing kinetic energies. This is due to the fact that our experimental spectra report also the contribution of surface plasmons, which is neglected in the MC calculations and whose relative importance diminishes with respect to bulk plasmons at higher values of the primary beam kinetic energy. It is worth noting that the normalization of the data at a common area of the elastic peak keeps the correct intensity ratios between the two main plasmon peaks.

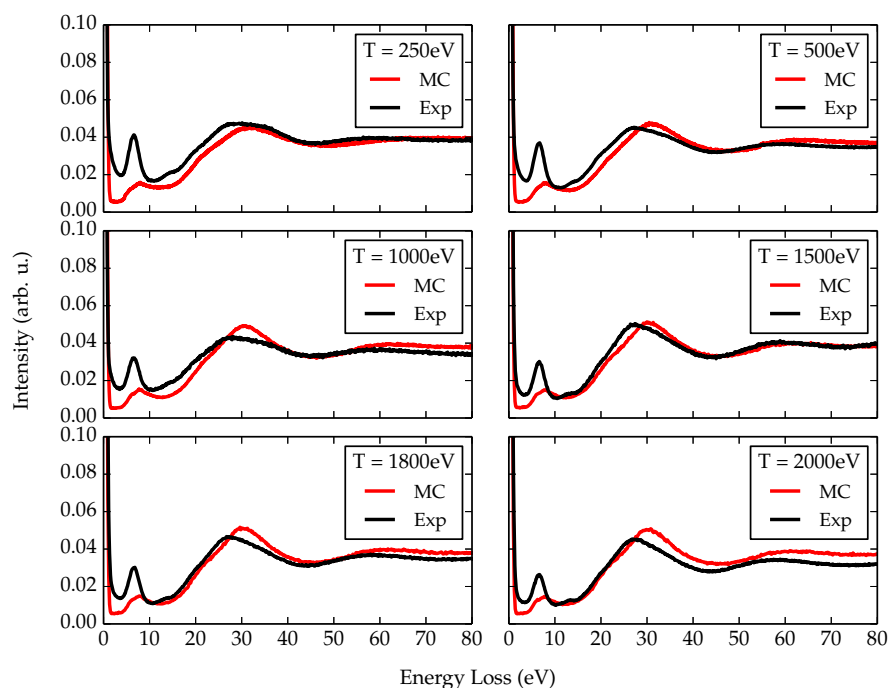


Figure 6: REELs of HOPG for several primary beam kinetic energies. Red lines show simulated spectra, while black curves report our experimental data<sup>21</sup>. The results are normalized at a common area of the elastic peak.

## Secondary Electron Spectrum

A quantitative understanding of SE spectra is crucial in imaging techniques. SE emission from graphite was thus assessed by MC simulations, using a kinetic energy of the incident beam ( $N = 10^6$ ) equal to 1000 eV. In the MC simulations the beam incident direction was chosen orthogonal to the sample surface, according to our experimental conditions (see experimental details section). In Fig. 7 we compare our MC calculations with the acquired experimental spectra. While the shape of the theoretical and experimental SE spectra is comparable, however the simulated spectrum has been shifted by 0.7 eV along the positive axis direction, in order to align the dominant emission peak.



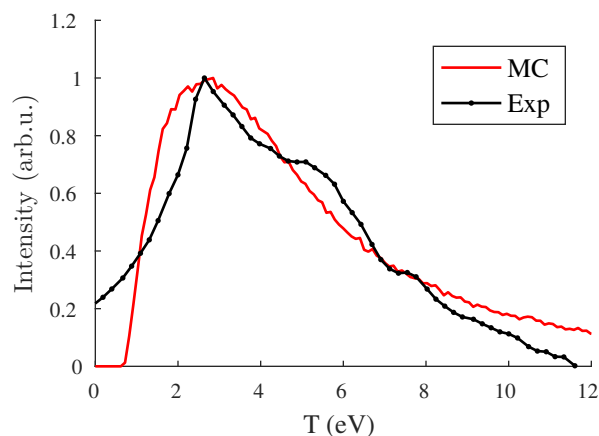


Figure 7: Secondary electron spectra of HOPG. Black line represents experimental data, while in red we report the theoretical spectrum. The data are normalized to a common height of the secondary electron emission peak.

## Conclusions

In this work, we performed Monte Carlo simulations, based on ab-initio input data of the energy-dependent dielectric function, of REEL and SE spectra of graphite, taking into account features related to the anisotropic structure of the target material. Graphite has indeed a layered structure and this must be considered in the treatment of the electron transport properties. In particular, the determination of the inelastic mean free path and of the energy loss was carried out by considering a linear combination of the dielectric properties along the two main orthogonal crystal directions (in-plane and out of plane).

In our model, the coefficients of this linear combinations depend on an anisotropy parameter  $f$  and on the angle between the transferred momentum  $\vec{q}$  and the surface normal vector  $\vec{c}$ . Our approach for including a dependence of the dielectric properties on the target anisotropy clearly improves the agreement between simulated and experimental REEL spectra. Indeed, spectral features are well reproduced by MC calculations for a value of the anisotropy parameter  $f = 0.6$ . This means that the energy loss along the  $\vec{q}||\vec{c}$  (inter-planar) direction contributes for 60% of inelastic collisions, while 40% of the spectral features are contributed by collisions along the  $\vec{q}\perp\vec{c}$  direction (in-plane). Furthermore, the MC simulations of secondary emission spectra, whose quantitative understanding is important in

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3 imaging applications, were carried out by using our anisotropic model and compared to in-  
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5 house recorded experimental spectra. We found a good agreement between theoretical and  
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7 acquired spectra with respect to the lineshape, that is the intensity of the spectral features,  
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9 while an energy shift was imposed to the theoretical data to reproduce the energy of the main  
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11 emission peak. These findings demonstrate the importance of considering properly-weighted  
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13 inter-planar and intra-planar interactions in the simulation of charge transport in layered  
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15 materials. Finally, the accuracy of our approach can be tested and possibly improved by  
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17 considering other descriptions of the ELF at low energies, such as using the Mermin dielectric  
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19 function presented by Garcia-Molina et al. in Ref.<sup>25</sup>. Moreover, the performance of these  
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21 models in the optical limit can be further improved by taking into account more rigorously  
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23 the exchange-correlation effects, particularly at low energy, according to Emfietzoglou et  
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25 al.<sup>26,27</sup>.

## 26 27 28 29 **Acknowledgement**

30  
31  
32 N.M.P. is supported by the European Commission H2020 under the Graphene Flagship Core  
33  
34 1 No. 696656 (WP14 "Polymer Composites") and under the FET Proactive "Neurofibres"  
35  
36 No. 732344. S.T acknowledge funding from No. 696656 WP14 "Polymer Composites" grant.  
37  
38 C.R. was funded by EPSRC (EP/N008065/1). Access to computing and storage facilities  
39  
40 owned by parties and projects contributing to the National Grid Infrastructure MetaCen-  
41  
42 trum provided under the program "Projects of Large Research, Development, and Innova-  
43  
44 tions Infrastructures" (CESNET LM2015042), is greatly appreciated ([https://www.metacen-](https://www.metacentrum.cz/en/)  
45  
46 [trum.cz/en/](https://www.metacentrum.cz/en/)). The authors gratefully acknowledge the Gauss Centre for Supercomputing for  
47  
48 funding this project by providing computing time on the GCS Supercomputer JUQUEEN  
49  
50 at Jülich Supercomputing Centre (JSC)<sup>28</sup>. Furthermore, the authors acknowledge FBK for  
51  
52 providing unlimited access to the KORE computing facility.  
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