# Plasmon Excitations in Carbon Onions: Model vs. Measurements

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**Abstract.** Non-relativistic local dielectric response theory has proven successful in the interpretation of Electron Energy Loss data of nanometer-size isotropic particles of different geometries. In previous work, we have adapted this model to take into account anisotropy as encountered in the case of carbon onions. We have shown that this anisotropy needs to be taken into account since important deviations with respect to an isotropic model can be observed. In this contribution, we report on the first energy filtered images of carbon onions and compare intensity profiles across the spheres to our calculations.

## INTRODUCTION

Electron Energy Loss Spectroscopy (EELS) in a High Resolution Transmission Electron Microscope (HRTEM) allows at the same time the characterization of the geometrical parameters and the investigation of the electronic properties of one single nanometer-size particle. This technique therefore does not rely on the necessity to dispose of high purity samples, which is interesting in the case of carbon nanostructures such as tubes or onions, since even though important progress has been made (1), the purity of the samples still is a problem. In fact, some measurements using this technique have already been reported, but a qualitative interpretation of the results has not yet been possible due to the lack of theoretical background.

Recent calculations (2) based on non-relativistic local dielectric response theory (3) have now evened a way for a detailed qualitative analysis of the experimental data. We report on the analysis of energy filtered transmission electron micrographs of carbon onions based on those calculations.

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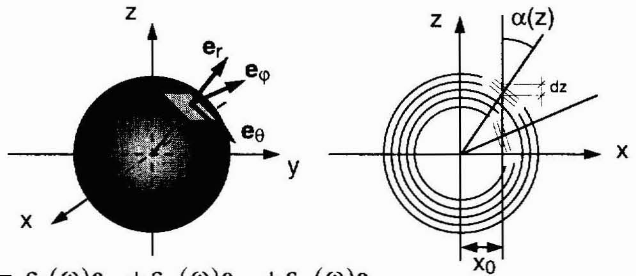
# MODEL OF THE EXCITATION OF PLASMONS

The model of the plasmon excitations in carbon onions was developed in the frame of non-relativistic local dielectric response theory (3). This approach consists in deducing surface and volume plasmon excitation probabilities from the dielectric tensor of the bulk material, taking into account the geometry of the particle. In the case of carbon onions, it is necessary to make an assumption about the dielectric properties of the particle. In our calculations, this was done following the scheme proposed by Lucas et al. (5) which consists in projecting the dielectric tensor of planar graphite into spherical coordinates (figure 1a). Accordingly it is assumed that locally the dielectric properties of a carbon onion can be described by the dielectric tensor of planar graphite.



$$\tilde{\varepsilon}(\omega) = \varepsilon_{\|}(\omega)\mathbf{e}_{rr} + \varepsilon_{\perp}(\omega)\mathbf{e}_{\theta\theta} + \varepsilon_{\perp}(\omega)\mathbf{e}_{\varphi\varphi}$$

**FIGURE 1.** (a) Model used for the electronic properties of a carbon onion. Locally, the electronic properties are supposed to be identical to those of planar graphite. (b) As the electron moves along its trajectory, it passes infinitely small layers of planar graphite oriented at an angle α with respect to the optical axis of the microscope.

Non-relativistic local dielectric response theory allows to calculate the excitation of the surface and volume plasmons separately, the total plasmon excitation probability being just the sum of the two. In our approach, the volume contribution is deduced from the excitation probability per unit path length of a planar sheet of graphite as calculated by Wessjohann (4). In fact, as the electron is travelling through the carbon onion, it crosses infinitely thin layers of graphite which continuously change their orientation as the electron moves on (see figure 1b). The volume plasmon excitation probability is therefore simply given by the integral of the orientation-dependent excitation probability given by Wessjohann along the path in the onion (Eq. 1). $q_p^2$ and $q_c^2$ are the projection of the transferred momentum on the plane perpendicular and on the direction parallel to the $c$-axis of the graphitic layer of thickness $dz$, respectively.

$$\frac{dP^{volume}(\omega)}{d\omega} = \frac{e^2}{4\pi\varepsilon_0\hbar v^2}\int_{-z_0}^{z_0} dz\int_0^{\theta_c}\theta d\theta\int_0^{2\pi} d\varphi\ \mathrm{Im}\left[\frac{-q_0^2}{q_p^2\varepsilon_\perp(\omega) + q_c^2\varepsilon_\perp(\omega)}\right] \qquad (1)$$

In order to calculate the surface plasmon excitation probability, the expression for surface plasmon excitation given in the review article by Wang has been used (3).

$$\frac{dP^{surface}(\omega)}{d\omega} = \frac{e}{\pi\hbar v^2}\int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dz\, Im\left\{ e^{i\omega(z'-z)/v} V^{ind}(\mathbf{r}, \mathbf{r}_0)\Big|_{\mathbf{r} = (x_0,\, 0,\, z')}\right\} \qquad (2)$$

$V^{ind}(\mathbf{r}, \mathbf{r}_0)$ is the induced electric potential at position $\mathbf{r}$ caused by a stationary electron located at position $\mathbf{r}_0$. It is the homogenous part of the solution of the equation $\nabla \bullet [\tilde{\varepsilon}(\omega)\nabla V(\mathbf{r}, \mathbf{r}_0)] = (e/\varepsilon_o)\delta(\mathbf{r}, \mathbf{r}_0)$. The details of how this induced potential is calculated can be found in ref. (2).

## MEASUREMENTS

The EELS measurements have all been carried out on a Philips CM 300 field emission microscope equipped with a Gatan Imaging Filter. The onions were produced *in situ* by intense irradiation of polyhedral closed shell graphitic particles (6) frequently found in the deposit of a conventional arc discharge used for the production of carbon nanotubes (7). Figure 2 shows a series of energy filtered images of a carbon onion of 12.5 nm radius (insets (b) through (e)).

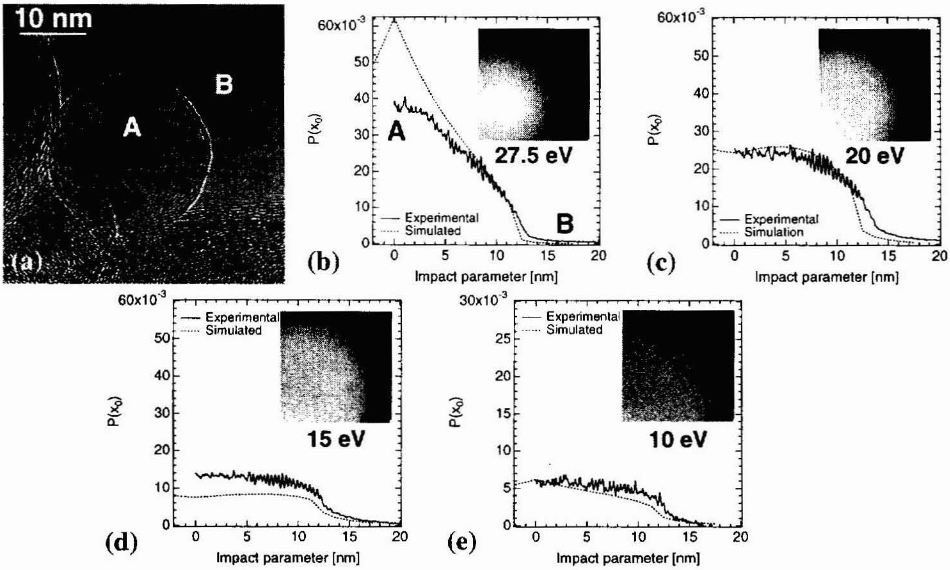


**FIGURE 2.** Non filtered HRTEM image (a) of a carbon onion of 12.5 nm radius on which the experiment was carried out. Figures (b) through (e) display intensity profiles across the energy filtered images shown in the inset (solid lines). The energy window was 4 eV wide and centred at the energies indicated in the corresponding figure. The profiles were taken from the centre of the sphere (A) to the point (B) indicated in the non-filtered image. Also shown are the simulated intensity profiles as obtained from the non-relativistic local dielectric response theory.

The experimental intensity profiles (solid lines) taken from points A to B are compared with the simulated profiles obtained from our model (dotted line).

It has to be noted that the observed intensities have not been scaled in any way in order to fit to our simulations, and that the simulations have been obtained without taking into account the characteristics of the electron beam (energy distribution and angular convergence). It can be seen that there is an excellent agreement between the experimental and theoretical curves at 10 and 20 eV, whereas at 15 eV the simulations slightly underestimate and at 27.5 eV they slightly overestimate the actual excitation probability. Further experiments and simulations are currently undertaken in order to clarify whether this difference between model and measurement arises from the experimental broadening of the plasmon excitation probability due to the finite energy resolution of the experimental setup or if it is due to either the effect of curvature of the layers or to the finite size of the particle.

## CONCLUSIONS

The preliminary analysis of our experimental data shows that non-relativistic local dielectric response theory is adapted for the interpretation of experimental electron energy loss data. A detailed analysis of the EEL spectra and energy filtered TEM images should therefore allow to determine the differences between the intrinsic properties of a carbon onion and those of planar graphite and hopefully contribute to a better understanding of the physical properties of those novel, intriguing form of carbon.

## ACKNOWLEDGEMENTS

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