# Electron inelastic mean free paths for carbon nanotubes from optical data

Ioanna Kyriakou,[1] Dimitris Emfietzoglou,[1,a)] Rafael Garcia-Molina,[2] Isabel Abril,[3] and Kostas Kostarelos[4]
[1]*Medical Physics Lab, University of Ioannina Medical School, 451 10 Ioannina, Greece*
[2]*Departamento de Física–CIOyN, Universidad de Murcia, Apartado 4021, E-30080 Murcia, Spain*
[3]*Departament de Física Aplicada, Universitat d'Alacant, Apartat 99, E-03080 Alacant, Spain*
[4]*Nanomedicine Lab, Centre for Drug Delivery Research, School of Pharmacy, University of London, London WC1N 1AX, United Kingdom*

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We present a simple model dielectric response function for both bulk and individual carbon nanotubes based on a parameterization of experimental optical data and analytic dispersion relations that account for dimensionality and linewidth broadening. The model is used to calculate electron inelastic mean free paths over a broad energy range of interest to various applications. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3167819]

The electron inelastic mean free path (IMFP) is a fundamental quantity to the study of various spectroscopic properties of solids and surfaces.[1] The biomedical use of carbon nanotubes (CNTs) as delivery systems of radionuclides to targeted cancer cells[2,3] or as highly sensitive miniaturized radiation detectors[4] requires that inelastic scattering data for CNTs over a broad energy range are available. Toward this aim we report here IMFP calculations for CNTs using the "optical data" method,[1] which offers a practical alternative to first-principles calculations[5,6] for electron energies much higher than the band gap, where the details of the band structure are less important. In this method, the key physical quantity is the energy-loss function (ELF), $\mathrm{Im}\{-1/\varepsilon(\omega,k)\}$, which depends on the energy ($\hbar\omega$) and momentum ($\hbar k$) dependent (macroscopic) dielectric function $\varepsilon(\omega,k)$. The ELF at $k\cong 0$ (optical limit) is determined from *experimental* optical data while its extension to $k>0$ where data are often not available (or limited) is obtained through theoretical dispersion relations.[1] By virtue of Bethe's theory, the method is most effective above ~200 eV where the optical limit of ELF prevails while its performance at lower energies will depend on the quality of the dispersion relations used. In general, results below ~50 eV are mostly qualitative. The method has proven useful for both bulk materials and solid surfaces.[7,8] Moreover, a macroscopic dielectric function can be suitable even for nanostructures as long as it is fair to consider their valence electrons as a continuum, that is, when the plasmon energy is much larger than the band gap energy.[9]

In the present work, the ELF at $k\cong 0$ is obtained from the electron-energy-loss sprectroscopy (EELS) measurements of Kuzuo and co-workers[10,11] on *bulk* samples of multiwalled CNTs (MWCNTs) (13–34 nm in diameter) and single-walled CNT (SWCNT) bundles. The Kuzuo data cover the important valence excitation range from 0 to 50 eV and, to a good approximation, have been reproduced numerous times both experimentally[12–15] and theoretically.[16–19] It is now clear that CNTs larger than ~20 nm in diameter, exhibit a well defined bulk plasmon peak at 20–24 eV corresponding to the $\pi+\sigma$ electrons, and a smaller one at 5–7 eV due to the $\pi$ electrons. For extending the Kuzuo data to higher energy losses (including the $K$ shell) where condensed-phase effects are less important, we use the National Institute of Standards and Technology (NIST) (Ref. 20) values for the photoabsorption coefficient ($\mu$) of carbon using $\mathrm{Im}(-1/\varepsilon)\approx\mathrm{Im}(\varepsilon)=c\mu/\omega$ ($c$ is the speed of light). We have parameterized the Kuzuo and NIST data by a linear superposition of Drude-type functions (atomic units are used)[21]

$$\mathrm{Im}\{-1/\varepsilon(\omega,k=0)\}_{\mathrm{data}}=\sum_i A_i\gamma_{i,0}\omega\{(\omega^2-\omega_{i,0}^2)^2+(\omega\gamma_{i,0})^2\}^{-1}\Theta(\omega-\omega_{c,i}), \quad (1)$$

where $A_i$, $\gamma_{i,0}$, and $\omega_{i,0}$ are the adjustable parameters that relate to the height, width, and position of the $i$th peak in the deconvolution of the experimental spectrum, and $\Theta$ is the step function. For the $K$ shell, the cutoff energy ($\omega_c$) is set at 285 eV and for the valence shells, at the onset of the EELS data (2–3 eV); the exact values are insignificant here. We have obtained a good representation of the experimental data (Fig. 1) while satisfying both the $KK$- and $f$-sum rules[1] to better than 1%. The Drude ELF [Eq. (1)] guarantees that for small $\omega_c$, the $f$-sum rule is fulfilled for all $k$ independent of the form of dispersion as long as it is satisfied at $k=0$. The $f$-sum rule violation at finite $k$ by the $K$ shell due to its large

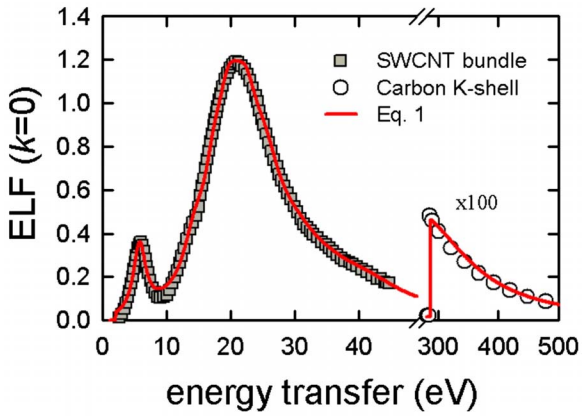


FIG. 1. (Color online) The parameterization of the Kuzuo (Ref. 11) and NIST (Ref. 20) data using Eq. (1) (the fit to the MWCNT data of Ref. 10 was of similar quality).

a)Electronic mail: demfietz@cc.uoi.gr.

 

$\omega_c$ is of no concern here since the *K*-shell contribution to the IMFP is less than 1%–2% in the present energy range.

To extend our study to individual SWCNTs, we make use of the observation[12–14,22–24] that *thin* MWCNTs with a diameter smaller than ~10 nm exhibit a redshifted $(\pi+\sigma)$ plasmon peak at 15–17 eV which coincides with Ritchie's "surface" plasmon frequency $\omega_s=\omega_p/\sqrt{2}$ ($\omega_p$ being the bulk plasmon frequency). To a first approximation, we can therefore model the dielectric response of an *individual* SWCNT by means of the *surface* ELF[7,8] $\mathrm{Im}\{-1/[\varepsilon(\omega,k=0)+1]\}$, where $\varepsilon(\omega,k=0)$ is the bulk dielectric function of Eq. (1).

Although various sophisticated approaches exist for the dispersion of bulk and surface excitations in CNT like systems,[25] in the present study we adopt a simple semiempirical approach in the spirit of the optical data method by taking advantage of the available EELS data at finite $k$ for bulk SWCNT samples[26] and *thin* bundles of vertically aligned (VA) SWCNTs.[27] The latter system is a reasonable approximation to individual SWCNTs because it lacks the typical dielectric screening properties of the bulk, as practically all the tubes in the bundle are on its surface with none in its interior.[28] For extending the ELF to $k>0$, we use the dispersion properties of the main $(\pi+\sigma)$ plasmon peak because the $\pi$ plasmon is generally more sensitive to band structure and CNT geometry, and therefore its distinct dispersion properties are difficult to be incorporated within the present method. This approximation should suffice for not too low electron energies where the contribution of the $\pi+\sigma$ plasmon is dominant. For bulk CNTs we use

$$\omega_i(k)=\sqrt{\omega_{i,0}^2+\alpha k+\beta k^2+k^4/4}, \tag{2}$$

where $\alpha=\sqrt{3/10}\omega_p v_F$ and $\beta=(3/5)v_F^2$ with $v_F$ being the Fermi velocity of the electron gas. The plasmon and Fermi energies deduced from the Kuzuo data are, respectively, 22.6 and 18.9 eV for the MWCNTs (Ref. 11) and 19.9 and 15.8 eV for the SWCNTs.[12] Equation (2) combines Ritchie's linear term[29] for boundary effects with the three-dimensional electron gas plasmon dispersion, and through the $k^4/4$ term approximately accounts for single-particle excitations at high $k$ where collisions are free-electron like.[30] For individual SWCNTs we use

$$\omega_i(k)=\sqrt{\omega_{i,0}^2/2+\omega_p^2(Rk)^{1/2}+k^4/4}, \tag{3}$$

where $R$ is the SWCNT radius (0.75 nm here) and $\omega_p$ is the value of the bulk SWCNTs (see above). The $k^{1/2}$ term in Eq. (3) follows from approximating the individual tube as a two-dimensional electron gas system with a nonzero long-wavelength frequency gap at the surface plasmon value.[31] Since the theoretical analysis of plasmon damping (at any dimension) is too complicated, a purely empirical relation was deduced from the ELF broadening of VASWCNTs (Ref. 27)

$$\gamma_i(k)=\gamma_{i,0}+a_1k+a_2k^2, \tag{4}$$

where $a_1=a_2=0.5$ Hartree. It can be seen from Fig. 2 that the dispersion relations of Eqs. (2)–(4) are adequate for both bulk and VASWCNTs while having the correct limiting behavior at $k=0$ and $k\to\infty$.

Having established an analytic form for the ELF over the $\omega$-$k$ plane and assuming that our systems are sufficiently long along the direction of $k$, we calculate the IMFP in the Born approximation by a double quadrature over both $\omega$ and $k$.[32] The IMFPs of the bulk samples (Fig. 3) are found to be overall similar with only a 10%–15% difference at high energies due to their different optical data. Substantially larger IMFPs are calculated for individual SWCNTs. This is primarily caused by the different dispersion properties of Eqs. (2) and (3) and less by the difference between the bulk and surface ELF at $k=0$. As expected for bulk samples, the TPP-2M formula[33] (with CNT parameters) and the NIST-SRD71 values for carbon[34] (at CNT density) agree with our calculations at high energies, but differ significantly in the region of the minimum where the results are more sensitive to the ELF at $k\neq 0$. Although we have used experimental data as much as possible, our calculations at low electron energies (below ~50 eV) are mostly qualitative due to the general shortcomings of the optical data method, e.g., the limitations of the Born approximation and the lack of band-structure details. A more accurate dispersion relation for the $\pi$ plasmon should also be considered at low electron energies given its increased contribution to the IMFP.

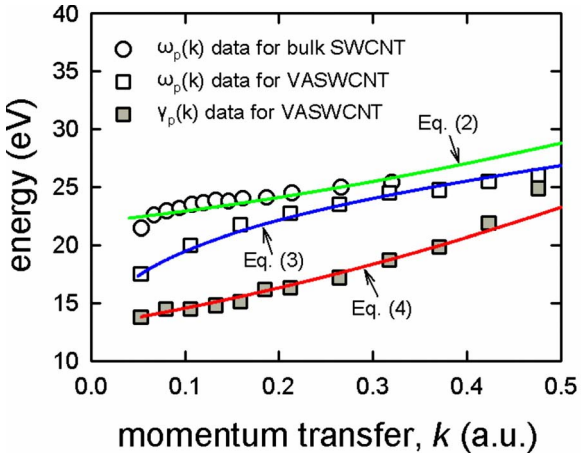


FIG. 2. (Color online) Comparison of our dispersion relations [Eqs. (2)–(4)] with experimental data for the $\pi+\sigma$ on bulk SWCNT samples (Ref. 26) and VASWCNTs (Ref. 27).

In conclusion, we have presented a simple model dielectric function analytic over the whole $\omega$-$k$ plane for different CNT systems based on the optical data method. The model is used to calculate electron IMFPs which should be reasonably accurate above ~50 eV for those systems which exhibit *bulklike* properties, such as SWCNT bundles and MWCNTs

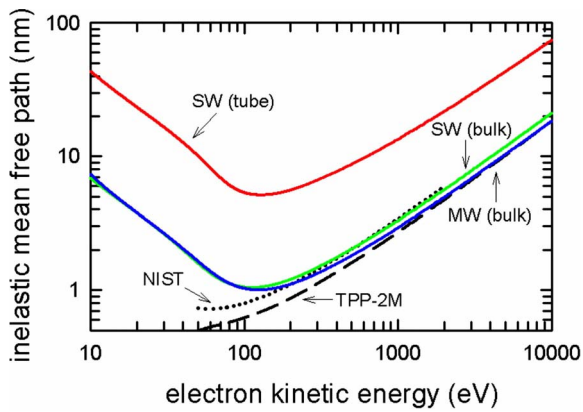


FIG. 3. (Color online) Calculated electron IMFPs for different CNT systems using Eqs. (1)–(4). IMFPs using the TPP-2M formula (Ref. 33) and the NIST SRD71 database (Ref. 34) are also presented.

with diameters larger than ~20 nm. Calculations for individual SWCNTs based on the surface-ELF approximation are also presented but they should be considered only qualitative. We expect that due to its simplicity, our model will facilitate calculations of other inelastic magnitudes for a broad energy range relevant to various applications where the type of CNTs examined play an important role.

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