Analytic expressions for the inelastic scattering and energy loss of electron and proton beams in carbon nanotubes

D. Emfietzoglou,1,a I. Kyriakou,1 R. Garcia-Molina,2 I. Abril,3 and K. Kostarelou4
1Medical Physics Laboratory, University of Ioannina Medical School, 45110 Ioannina, Greece
2Departamento de Física–CIObyN, Universidad de Murcia, E-30100 Murcia, Spain
3Departamento de Física Aplicada, Universidad d’Alacant, E-03080 Alacant, Spain
4Nanomedicine Laboratory, Centre for Drug Delivery Research, School of Pharmacy, University of London, London WC1N 1AX, United Kingdom

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We have determined “effective” Bethe coefficients and the mean excitation energy of stopping theory (I-value) for multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotube (SWCNT) bundles based on a sum-rule constrained optical-data model energy loss function with improved asymptotic properties. Noticeable differences between MWCNTs, SWCNT bundles, and the three allotropes of carbon (diamond, graphite, glassy carbon) are found. By means of Bethe’s asymptotic approximation, the inelastic scattering cross section, the electronic stopping power, and the average energy transfer to target electrons in a single inelastic collision, are calculated analytically for a broad range of electron and proton beam energies using realistic excitation parameters. © 2010 American Institute of Physics. [doi:10.1063/1.3463405]

I. INTRODUCTION

Beams of charged particles (i.e., electrons, protons, or heavier ions) represent an established tool for the controlled modification of materials and have already been used for tailoring the physical and chemical properties of carbon nanotubes (CNTs) (Refs. 1 and 2) representing, in effect, another postsynthetic, “constructive destruction” sorting approach.3 However, in order to optimize the use of charged-particle beams and to predict radiation damage in space or nuclear technology applications, it is important that their interactions with CNTs are well understood and accurately quantified. Most studies so far have concentrated on the nuclear stopping of CNTs due to the elastic scattering of charged particles by target atoms leading to knock-on displacement of carbon atoms from the CNT lattice.4 This is the dominant radiation damage mechanism for slow ions below ~10 keV/u and electrons above the CNT knock-on threshold of ~80 keV.5 In contrast, little is known on the electronic stopping of CNTs due to the inelastic scattering of charged particles by target electrons, despite the fact that electronic excitations can effectively mediate materials modification and cause radiation damage through (mainly) beam-stimulated local chemical reactions.2,5

There exist several recent theoretical studies of the electronic energy loss of charged particles in CNTs.6–15 The approaches can be divided to those using Bloch’s hydrodynamic approximation6–9 and those employing the dielectric response theory either in the Bohm–Pines random-phase-approximation10,11 or in the semiclassical Drude approximation.12–15 Both approaches have been successfully applied to a variety of low-dimensional systems and carbon nanostructures, in particular. Dielectric models are known to be particularly effective in describing plasmon excitations in an electron gas whereas hydrodynamic models, although perhaps more qualitative in some respects, are capable of handling boundary effects due to the presence of different dielectric media. However, due to the considerable amount of numerical work involved, both approaches are usually restricted to the study of individual CNTs [most often isolated single-walled CNTs (SWCNTs)]. Thus, for practical calculations and data analysis concerning the irradiation of bulk CNT systems (e.g., bundles) or macroscopic samples (e.g., thin films) one would wish to have a simpler approach of wider applicability valid over a wide range of energies of the incident charged particle. Due to the absence of such a simple model, bulk graphite excitation properties are commonly used for describing the inelastic interaction between the charged-particle beam and the CNT.

The aim of the present work is to provide realistic excitation parameters for multiwalled CNTs (MWCNTs) and SWCNT bundles in order to enable the inelastic scattering cross section, the electronic stopping power, and the average energy transfer to target electrons in a single inelastic collision to be calculated analytically as a function of charged-particle beam energy. This is accomplished within the theoretical framework of the Bethe theory.16 Compared to previously used methods,6–15 the main advantage of the Bethe theory is that it offers the possibility of expressing the above magnitudes in a strikingly simple analytic form applicable over a wide range of beam energies within, of course, the limits of validity of the plane-wave Born approximation (PWBA). Thus, it is feasible using a simple method to address practical problems associated, for example, with irradiation experiments using kilo-electron volt electron beams from scanning electron microscope or transmission electron microscope and megaelectron volt protons relevant to space applications. For economy of space all expressions are given in their nonrelativistic form and, therefore, pertain to the longitudinal part of the interaction. In their present nonrelativistic...
II. INELASTIC CROSS SECTIONS

The Bethe theory provides an asymptotic expansion for the inelastic scattering cross section of PWBA in powers of \( T^{-1} \) (\( T \) is proportional to the square of the charged-particle velocity) with coefficients that depend solely on materials properties. Hereafter the use of the Bethe asymptotic expansion to \( T^{-1} \) order will be called the Bethe approximation. Then, the probability per unit path length that a (nonrelativistic) charged particle will transfer energy \( W \) to the target can be expressed in the Bethe approximation as follows:

\[
P_W(eV^{-1} \text{ nm}^{-1}) = 3.01 \ln(-1/e_W) T(eV)^{-1} \ln(c_W T(eV)/Ry),
\]

where \( Ry \) is the Rydberg constant, \( T = mv^2/2 \) with \( m \) being the electron rest mass and \( v \) the projectile velocity, and \( e_W \) is the dielectric response function of the target at vanishing momentum transfer or optical limit (\( q \approx 0 \)). The value of the constant on the right-hand-side of Eq. (1) comes from: \((2 \pi a_0)^{-1} = 3.01 \text{ nm}^{-1} \) where \( a_0 \) is the Bohr radius. Note that, in the present units, the \( P_W \) of Eq. (1) is equivalent to the differential inverse inelastic mean free path. The \( \text{Im}(-1/e_W) \) is the so-called energy loss-function (ELF), also at the optical limit, which describes the excitation spectrum of the material by inelastic charged-particle scattering at nearly forward angles. The Bethe coefficient \( c_W \) is a complicated function of \( W \) that depends on the value of ELF at finite \( q \) and, generally, is of the order of unity.\(^{16} \) Evidently, the use of Eq. (1) depends upon the evaluation of \( \text{Im}(-1/e_W) \) and \( c_W \) which are both excitation properties of the material independent of the charge, velocity, or mass of the particle.

Although the dielectric response of individual CNTs is anisotropic (like graphite), for random (nonparaxial) charged particle trajectories both the in-plane and out-of-plane excitations are involved due to the cylindrical geometry. In this case, the use of a macroscopic (continuum) dielectric response function, as the one employed here, seems justified. Obviously, this approximation will also suffice for bulk or macroscopic samples containing nonaligned CNTs (e.g., bundles). More generally, the present approach should be reasonably valid for those cases where the contribution of in-plane and out-of-plane excitations is comparable, e.g., as in angle-integrated electron-energy loss spectroscopy (EELS).\(^{17} \) To determine the \( \text{Im}(-1/e_W) \) of the examined CNT systems over the broad excitation range relevant to the inelastic interaction of energetic charged-particle beams, we proceed as follows. Due to the large energy difference between valence-electron and core-electron excitations, the total ELF (at \( q = 0 \)) can be approximated by the following sum:

\[
\text{Im}(-1/e_W) = \text{Im}(-1/e_W)_v + \text{Im}(-1/e_W)_K,
\]

where “\( v \)” and “\( K \)” denote the valence and K-shell contributions, respectively. As first suggested by Powell,\(^{18} \) the valence contribution to the ELF, \( \text{Im}(-1/e_W)_v \), can be derived from experimental optical data which ensure a realistic, material-specific representation of the excitation spectrum. In the present work we adopt our previously developed Drude parameterization\(^{19} \) of the experimental EELS data measured from relatively thick MWCNTs (~21–44 walls and 13–34 nm in diameter)\(^{20} \) and large SWCNT bundles\(^{21} \) over the valence excitation range (~0–50 eV). \textit{Ab initio} time-dependent density-functional-theory calculations\(^{22} \) of the ELF of SWCNTs at vanishing momentum transfer (optical limit) over the valence excitation range have confirmed the general characteristics of the EELS data.\(^{21} \) In particular, it was shown that at the long length scales associated with the optical limit the position of the \( \pi + \sigma \) plasmon peak, the main energy-loss channel of the system, sensitively depends upon screening effects due to intertube interactions. These screening effects lead to a shift of the peak to higher energy losses and a pronounced difference between \( \text{Im}(-1/e_W)_v \), and the optical absorption spectrum, \( \text{Im}(-1/e_W)_v \). As expected, this difference vanishes for nearly isolated tubes at large intertube separations where \( \text{Im}(-1/e_W)_v \rightarrow \text{Im}(-1/e_W)_K \).

For the K-shell contribution which sets in at ~285 eV (approximately the carbon K-edge) and for which the approximation \( \text{Im}(-1/e_W)_K \approx \text{Im}(-1/e_W)_K \) safely holds, we improve upon our previous calculation\(^{19} \) using the relation \( \text{Im}(-1/e_W)_K = \text{const.}(N/Z)W^{-1}(\xi dH_N^L/dW) \) where const. \( = 8\pi^2a_0^2Ry^2, N/Z \) are the target electronic density and atomic number, respectively, \( dH_N^L/dW \) is the optical limit of the scaled hydrogenic generalized-oscillator-strength (GOS) of carbon,\(^{24} \) and \( \xi = 1.026 \) is a normalization factor deduced from first-principles atomic calculations.\(^{24} \) In Fig. 1 it is clearly shown that the present model for the K-shell significantly improves the asymptotic behavior at large \( W \) of the Drude K-shell model used previously,\(^{19} \) as judged from the comparison with the x-ray data from the National Institute of Standards and Technology (NIST).\(^{25} \) We should note that any variation in the shape of the carbon K-edge in different carbon structures\(^{26} \) is too small to be of any significance for the present calculations where the magnitudes of interest depend mainly upon integrals of the ELF over a broad excitation range.

The overall internal consistency of our ELF model is tested by two important sum rules,\(^{27} \) namely, the Kramers–
König (KK) and f-sum rules that read, respectively, \( \Pi_{eff} = (2/\pi) \int_{0}^{\infty} W^{-1} \text{Im}[-1/e_W]dW + \text{Re}(1/e_W0) \), where \( \text{Re}(1/e_W0) = 1/e_1 \) with \( e_1 \) being the limiting value of \( e_W \) as \( W \rightarrow 0 \), and \( Z_{eff} = (2Z/\pi\hbar^2)^{1/2} \int_{0}^{\infty} W \text{Im}[-1/e_W]dW \), where \( E_p = \hbar \sqrt{4\pi Ne/m} \) is the free-electron plasmon energy of the material. From the EELS data\(^{20,21} \) for the two systems examined we deduce the values: \( E_p = 27.8 \text{ eV} \) and \( e_1 = 4.88 \) for MWCNTs, and \( E_p = 24.4 \text{ eV} \) and \( e_1 = 4.09 \) for SWCNT bundles. It is important that both sum rules are satisfied because, as it is apparent from their definition as well as from Fig. 2, the value of \( \Pi_{eff} \) is sensitive to small \( W \) (below \( \sim 50 \text{ eV} \)) whereas that of \( Z_{eff} \) to intermediate and large \( W (\sim 50–5000 \text{ eV}). \) Thus, in effect, the KK and f-sum rules are complementary. As shown in Fig. 2, for \( W \rightarrow \infty \) we obtain (to better than 1%) the correct limiting values \( Z_{eff} \approx 6 \) and \( \Pi_{eff} \approx 1. \)

The form of Eq. (1) suggests that \( \text{Im}[-1/e_W] \) suffices at the limit of large \( T \) where \( P_W \) goes asymptotically as \( T^{-1} \ln(T). \) To go beyond the optical approximation the coefficient \( c_W \), associated with finite \( q \) features in the ELF, must be determined. However, since an analytic expression for \( c_W \) is not feasible, we adopt an approximate procedure and determine an “effective” Bethe coefficient \( c_{tot} \) (independent of \( W \)) from the relation \( P_{tot} = \int P_w dW \), where \( P_{tot} \) is the total inelastic scattering cross section in dimensions of inverse length (equivalent to the inverse inelastic mean free path). The \( P_{tot} \) is calculated numerically within the PWBA where the key material property is the momentum-dependent ELF. The latter is calculated from the present \( \text{Im}[-1/e_W] \) extended to arbitrary \( q \) values by semiphenomenological dispersion relations\(^{19} \) and the analytic properties of the GOS model.\(^{23} \) The use of extended optical-data models is known to give reasonably accurate results within the range of validity of PWBA, as exemplified by the widespread usage\(^{28,29} \) of the Penn\(^{30} \) and Ashley\(^{31} \) models (among others\(^{32,33} \)). In the present work, however, we go beyond the standard dispersion approximations for unbound (infinite) media by accounting for finite-size and linewidth broadening effects in CNTs as discussed in Ref. \(^{19} \). The values of \( c_{tot} \) which provide the best overall fit to the numerical \( P_{tot} \) data are \( c_{tot} = 0.80 \) for MWCNTs and \( c_{tot} = 0.88 \) for SWCNT bundles. Both values are considerably lower than the corresponding values found for the three allotropes of carbon using Penn’s algorithm;\(^{34} \) \( c_{tot} = 1.415 \) for diamond, \( c_{tot} = 1.59 \) for graphite, and \( c_{tot} = 1.59 \) for glassy carbon. Having determined \( c_{tot} \), it is then straightforward using Eq. (1) to obtain an analytic expression for \( P_{tot} \) as a function of beam energy in the Bethe approximation:

\[
P_{tot}(\text{nm}^{-1}) = 3.01T(\text{eV})^{-1}b_{tot}(\text{eV})\ln(c_{tot}T(\text{eV})/\text{Ry}),
\]

where the Bethe coefficient \( b_{tot} = \int_{0}^{\infty} \text{Im}[-1/e_W]dW \) depends upon an integral over the complete ELF at \( q = 0. \) Using the present \( \text{Im}[-1/e_W] \) we obtain \( b_{tot} = 27.9 \text{ eV} \) for MWCNTs and \( b_{tot} = 23.9 \text{ eV} \) for SWCNT bundles. In terms of the perhaps more familiar dipole-matrix-elements squared (for all electronic excitations) \( M_q^2 = (2\text{Ry}/\pi\hbar^2)^2b_{tot}, \) we obtain \( M_0^2 = 1.88 \) for MWCNTs and \( M_0^2 = 2.09 \) for SWCNT bundles. In comparison, the corresponding values for the three allotropes of carbon determined also from experimental optical data are;\(^{34} \) \( M_0^2 = 1.552 \) for diamond, \( M_0^2 = 2.038 \) for graphite, and \( M_0^2 = 1.690 \) for glassy carbon. From inspection of Eq. (2) it is seen that the magnitude of \( P_{tot} \) for \( T/\text{Ry} \gg c_{tot} \) is determined primarily by the value of \( b_{tot} \) (or \( M_0^2 \)) while the details of its energy variation at not too large \( T \) will depend upon \( c_{tot}. \)

In Fig. 3 we compare the results obtained from the analytic Bethe expression, Eq. (2), against the numerical calculations of \( P_{tot} \) in the PWBA as described above. It is clear from Fig. 3 that the above determined values for the Bethe coefficients, \( b_{tot} \) and \( c_{tot} \), render Eq. (2) in good agreement with the numerical data almost down to the cross section maximum. Specifically, for electrons the difference between the analytic and numerical results is less than \( \sim 3\% \) above \( 500 \text{ eV} \) rising to \( 10\%–15\% \) at \( 200 \text{ eV} , \) whereas for protons it is less than \( 3\% \) above \( 100 \text{ keV} \). Thus, Eq. (2) with the present Bethe coefficients can be safely used almost over the full range of validity of the PWBA. For extending further the application of Eq. (2) to even lower \( T \) one would need to determine \( P_{tot} \) to the order \( T^{-2} \). However, due to the inherent limitations of the PWBA, the uncertainty associated with the
numerical $P_{\text{tot}}$ values below the maximum increases rapidly so the usefulness of such an effort is questionable. Also, it should be pointed out that the conventional determination of $c_{\text{tot}}$ through a Fano plot analysis of the high-energy asymptotic Bethe region would have naturally restricted the reliability of Eq. (2) to significantly higher beam energies. In contrast, with the present approach, Eq. (2) is now useful over a broader energy range. Although relativistic corrections to the electron calculations can amount to $\sim 10\% - 20\%$ in the range 30–100 keV, the inclusion of such corrections is inconsequential here since they will apply equally to both the Bethe and PWBA calculations.

### III. ELECTRONIC ENERGY LOSS

The Bethe asymptotic expansion holds for any momentum integrated cross section. Then, in the Bethe approximation (i.e., to order $T^{-3}$) the electronic stopping power, defined as the mean energy loss per unit path length due to inelastic collisions with target electrons, can be expressed in the following analytic form:

$$S(eV/\text{nm}) = 13.0N(e/\text{nm}^2)T(eV)^{-1}\ln(aT(eV)/\langle I(eV)\rangle),$$

where $a = 1.166$ for electrons and $a = 4$ for protons. The value of the constant on the right-hand-side of Eq. (3) comes from: $8\pi\rho_{0}R_{0}^{2} = 13.0(\text{nm eV})^2$. The $I$-value or mean excitation energy of the material is the only nontrivial parameter in Eq. (3) defined by an energy-weighted integral over the ELF as follows:

$$I = \lim_{W\to\infty} \exp \left\{ \int_{0}^{W} W \ln(W) \ln(-1/eW) dW \right\}.$$  

A plot of the exponential on the right-hand-side of Eq. (4), or cumulative mean excitation energy, $I_W$, is presented in Fig. 4. Clearly, as found for other materials, the limiting value of $I_W$ is reached at relatively high $W$ (at least approximately ten times the K-edge) with the K-shell having the dominant contribution due to its large binding energy. This realization has two effects: first, it makes the $I$-value particularly sensitive to the model used for $\ln(-1/eW)$ and, second, restricts the reliability of Eq. (3) to values of $T$ much larger than the K-edge, unless it is supplemented by a so-called shell-correction term (of order $T^{-3}$) related to the $q$-dependence of ELF

For $W \to \infty$ we obtain $I = 85.8$ eV for MWCNTs and $I = 78.4$ eV for SWCNT bundles. Since the $I$-value depends upon the spectral distribution of $\text{Im}[-1/eW]$, the larger $I$-value for MWCNT is consistent with the observation of a blueshift in the plasmon energy with increasing number of walls. In comparison, the ICRU (Ref. 38) recommended value for graphite is $I = 78$ eV while recent estimates for the three allotropes of carbon based on experimental optical data give: $I = 89.4$ eV for diamond, $I = 76.5$ eV for graphite, and $I = 102.5$ eV for glassy carbon. Although a difference in the $I$-value of the order of 10 eV has a relatively small influence on the magnitude of $S$ (for $T \gg I$) it can still have important practical consequences due to its impact on the absolute magnitude of the penetration range and, accordingly, on the depth-dose profile (and the Bragg peak position in proton beam irradiation) over distances comparable to the dimensions of the irradiated CNT systems.

The average energy transfer, $W_{\text{av}}$, to the electronic subsystem of CNTs in a single inelastic collision can also be calculated analytically within the Bethe approximation from:

$$W_{\text{av}} = \frac{S}{P},$$

where $P = P_{\text{tot}}$ and $S$ are obtained from Eqs. (2) and (3), respectively. Recently, $W_{\text{av}}$ has been shown to be an important parameter for understanding the role of electronic excitations in the microscopic mechanism of defect production in CNTs by charged-particle beams. A plot of $W_{\text{av}}$ as a function of beam energy is presented in Fig. 5.

Interestingly, the observed difference of 5–10 eV between MWCNTs and SWCNT bundles is comparable to the postulated threshold for "direct" inelastic damage to CNTs. A difference of several electron volts can also have important consequences to secondary electron emission applications.

### IV. CONCLUSION

In the present work, we have determined "effective" Bethe coefficients ($b_{\text{tot}}$, $c_{\text{tot}}$) and the mean excitation energy ($I$-value) of stopping power theory for MWCNTs and SWCNT bundles based on an improved ELF model deduced from experimental optical data for valence-electron excitations and atomic properties for core-electron excitations. Noticeable differences between MWCNTs, SWCNT bundles, and the three allotropes of carbon (diamond, graphite, glassy...
carbon) are found. The above excitation parameters enable, within Bethe’s asymptotic approximation, the inelastic scattering cross section, the electronic stopping power, and the average energy transfer to the electronic subsystem in a single inelastic collision to be calculated analytically for a broad range of electron and proton beam energies. Using the simple $z^{2}$-scaling (where $z$ is the charge of the particle) of the PWBA, the expressions can also be used for other light ions (e.g., $\alpha$-particles). Moreover, due to their simplicity and analytic properties they can be directly usable for Monte Carlo simulation of the inelastic interactions of kiloelectron volt electron and megaelectron volt proton beams in bulk, macroscopic samples containing MWCNTs or SWCNT bundles. It is also envisioned that, by employing excitation parameters specific to CNTs, the present expressions would provide a more realistic model for the inelastic interaction of charged-particle beams with CNTs and thus, improve upon the widely used practice of using beam-bulk graphite interaction models.

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