Interactions of ions with carbon nano-structures

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Abstract. We review some aspects of modeling interactions of charged particles with carbon nano-structures where dynamic response of carbon valence electrons plays prominent roles. Specifically, we evaluate the effects of plasmon excitations on the image and stopping forces on fast ions and dipolar molecules channeled through carbon nanotubes, as well as the effects of single-electron excitations in graphene’s \( \pi \) band on the image and stopping forces on slow ions grazingly scattered from a supported graphene.

1. Introduction
Investigation into the properties of fullerene molecules, carbon nanotubes, and the recently contrived graphene has been growing at a relentless rate for a decade or so, promoting carbon nano-structures among the hottest topics in Physics [1]. While interactions with particle beams have been an important part of this research endeavor in the context of various spectroscopic techniques (such as TEM, EELS, ...), the use of energetic electron and ion beams has recently emerged as a novel engineering tool for modification of structure and properties of carbon nano-structures [2]. Namely, while the irradiation of solids by energetic particles is usually perceived to cause undesired and uncontrolled disorder, recent experiments have demonstrated that many properties of carbon nano-structures can be tailored with high precision using particle beams. Moreover, carbon nano-structures exhibit exceptional propensity towards self-organization and self-assembly following such irradiation [2].

Examples of recent experimental demonstrations of the effects of ion irradiation of carbon nano-structures include: doping and chemical functionalization, creation of local defects (requiring typical energy transfer of some 20 eV per carbon atom) which can change electrical and thermal conductance, creation of various kinds of inter-junctions which can affect electrical and especially mechanical properties of carbon nanostructures, particularly for their use in composite materials, etc. [2]. As an illustration, one can mention fabrication of a nanotube-based electronic device, where focused ion beam of 30 keV Ga\(^+\) ions was used to create a pair of defect-rich regions, some 50 nm apart, in a single-wall carbon nanotube lying on a SiO\(_2\) substrate, thus giving rise to a quantum dot with well defined current-voltage characteristics [3].

In the context of using energetic ion beams, it is obviously most important to understand, and make effective use of the energy transfer to carbon nano-structures, especially in view of the traditional concept of separation between the so-called electronic stopping and nuclear stopping [4]. This is particularly important because current experiments employ a very wide range of ion energies, going from several tens of eV to some MeV. However, the concept of electronic stopping power, which is based on averaging over many ion trajectories in solid targets, probably needs to be revised for nano-objects where such statistical approach cannot be applied with confidence. Nevertheless, given that carbon nano-structures are excellent heat and charge conductors, one can assert that structural changes due to ion irradiation
must be dominated by knock-on atomic displacements which are most efficient at the low end of the irradiation energy range. Depending on the ion mass, maximum cross section for processes giving rise to defect production in carbon nano-structures occurs at the \(10^2 - 10^3\) eV energy range [5].

While the above applications of ion beams to carbon nano-structures require ion impacts with high probability of head-on collision with carbon atoms, the presence of large hollow regions in those structures and a high degree of their ordering and alignment present unique possibilities for achieving the effect of ion channeling [6]. Since this effect requires a sequence of ion collisions on carbon atoms with large impact parameters, one expects strong directional effects during ion passage through regular assemblies of carbon nano-structures. For example, directional effects in interactions of energetic ions with highly-oriented pyrolytic graphite (HOPG) have been recently studied experimentally in several contexts, including ion and molecule implantation in HOPG [7], ion channeling through HOPG [8], and secondary electron emission from HOPG induced by fast ions [9] and molecules [10]. While HOPG can be considered as layered material consisting of stacks of individual graphene sheets separated by about 3.35 Å, there exist other attractive possibilities for ion (and electron) channeling through carbon nano-structures exhibiting well aligned and ordered hollow regions of similar size. Those structures include fullerite, a regular crystalline structure made of \(C_{60}\) molecules, and the inter-tube regions inside the so-called ropes (or bundles) of carbon nanotubes forming hexagonal super-lattice. Ion channeling through nanotube ropes has attracted considerable theoretical interest in the past several years [11, 12].

Moreover, channeling through the interior of individual single- and multi-walled carbon nanotubes, possibly held in a matrix of some other material, has also been studied in great detail [11, 14, 15], with a view to possible applications in accelerator physics [13], or to explore processes in nanotubes analogous to those occurring during ion and molecule transport through nano-capillaries in solids [16, 17, 18]. While channeling through carbon nanotubes has been studied mostly theoretically so far, as reviewed in Refs. [11, 14, 15, 12], a few developments have been reported very recently on the experimental side, demonstrating the feasibility of both ion- [19], and electron channeling through carbon nanotubes [20].

Compared to the classical area of ion channeling through single crystals [6], one expects that channeling through nano-structures made of carbon nanotubes offers several advantages, such as, wider channels implying weaker de-channeling and consequently longer channeling distances, broader ion beams that can be used for channeling through nanotube ropes, wider acceptance angles (up to \(\sim 0.1\) rad) and consequently lower minimum required ion energies (\(< 100\) eV), and full three-dimensional (3D) control of beam deflection by bent nanotubes. As regards possible applications of ion channeling through carbon nanotubes, one can think of its use as a diagnostic tool for analyzing nanotube-based structures. Moreover, one should mention creation and transportation of highly focused nano-beams, ion implantation at the nano-scale for the next-generation electronic devices, targeted drug delivery and radiation therapy at the cellular level in medicine, as well as extraction, steering and collimation of ion beams at high-energy particle accelerators.

Going beyond carbon nanotubes, and having in mind that the special scattering geometry under channeling conditions eliminates head-on collision with carbon atoms, it is tempting to further pursue research into interactions of particle beams with graphene under glancing incidence to better understand their electronic response. Besides obvious interest in such processes owed to the fact that graphene is a building block of all carbon nano-structures, one can, and should also explore interesting parallels with the phenomena discovered in the well-known experiments on grazing scattering of ions from solid surfaces [21]. Moreover, one can speculate on the kinds of defect formation in graphene by analogy with the recent studies of nanostructures formed on crystal surfaces due to the impact of highly-charged ions [17].

As regards theoretical modeling and simulation of ion interactions with carbon nano-structures, various methods have been used depending on ion energies and incident trajectories. For ion channeling in the axial direction through structures made of carbon nanotubes at relativistically high energies (\(\sim 1\) GeV), both classical and quantum ion trajectories have been investigated on the basis of Lindhard’s continuum approximation for the strings of carbon atoms in the walls of individual carbon nanotubes.
2. Particle channeling through a carbon nanotube

As a prototype for modeling collective electron excitations, we consider channeling of a fast, point charge distribution through a straight, infinitely-long single-wall carbon nanotube in vacuum, having the radius \( a \). Since ion trajectories do not interact closely with individual carbon atoms in the target, but rather “integrate” over large numbers of such atoms each time when they “bounce” off the nanotube wall, it is reasonable to assume that the ion-core lattice of the nanotube is described by a two-dimensional, cylindrically shaped continuous distribution of rigid positive charges. Such two-dimensional jellium model is particularly suitable for describing ion channeling through chiral carbon nanotubes, where strings of carbon atoms “swirl” around the nanotube axis.

Furthermore, electron excitations in so described carbon nanotubes may be modeled by assuming that carbon valence electrons form a two-dimensional electron gas, which can be described quantum-mechanically in the so-called random phase approximation (RPA) \([25]\), or semiclassically by using the hydrodynamic model \([26]\). We note that this model can be applied to all four valence electrons in carbon nano-structures, both electron transfer and dynamic response of the target electrons may bring new and interesting effects which do not necessarily play prominent roles at very high or very low ion energies. Those effects become especially prominent under channeling conditions and/or for ion incidence with large impact parameters onto carbon nano-structures, where one can identify effects of the dynamic image force on the incident ions, as well as inelastic processes giving rise to ion energy losses to the collective, or plasmon excitation in carbon nano-structures \([15]\). Moreover, regularity of ion trajectories under channeling conditions still enables the use of continuum models for interaction potentials at such energies, and consequently restores the concept of stopping power. In this article, we shall review several recent developments in modeling of such phenomena.

Finally, at low ion energies \( (\sim 1 \text{ keV}, \text{ or less}) \), strong interactions with individual carbon atoms are likely, even under channeling conditions, and one has to obtain ion trajectories using some version of the Molecular Dynamics (MD) simulation \([5, 22, 23, 24]\). Typically, such simulations solve classical equations of motion for incident ions using various model interaction potentials for ion interaction with individual carbon atoms, depending on ion energy. On the other hand, the use of the so-called Brenner type II reactive bond-order empirical potential for interactions between carbon atoms enables accurate determination of defect formation, its transport across the target, as well as the self-assembly of target after the collision cascade is over. The most difficult question to resolve at low ion energies is the role and significance of electronic processes. In that context, it has been shown recently, by using the Time-dependent Density-functional Theory (TDDFT) for target electrons, that the Born-Oppenheimer approximation and the binary-collision approximation underlying MD simulations are applicable for ion interactions with carbon nano-structures at low energies \([4]\).
We further assume that the electron gas on the nanotube is distributed in an infinitesimally thin layer with number density per unit area $n_0 + n_1(r, t)$ at the position $r = \{r = a, \varphi, z\}$ on the surface of the cylinder. Here, $n_0$ is the equilibrium number density compensating the positive ionic background and $n_1(r, t)$ is the perturbation of the electron number density due to the external potential. In the linear response regime, one may introduce a polarization function of the 2D electron gas, $\chi(r', t - t') = \chi(\varphi - \varphi', z - z', t - t')$, and express the first-order perturbation of the electron number density $n_1(r, t)$ in terms of the external potential impressed on the nanotube surface at points $r' = \{r' = a, \varphi', z'\}$ and time $t'$, as

$$n_1(r, t) = \int dr' \int dt' \chi(r, r', t - t') \Phi_{\text{ext}}(r', t').$$

(2)

Invoking the jellium approximation, one can define the Fourier transform for an arbitrary function $A(r, \varphi, z, t)$ as

$$A(r, \varphi, z, t) = \sum_m \int \frac{dk d\omega}{(2\pi)^3} e^{i m \varphi} e^{i k z} e^{-i \omega t} \tilde{A}(r; m, k, \omega),$$

(3)

and rewrite (2) as

$$\tilde{n}_1(m, k, \omega) = \tilde{\chi}(m, k, \omega) \tilde{\Phi}_{\text{ext}}(a; m, k, \omega),$$

with $\tilde{\chi}(m, k, \omega)$ obtained form the hydrodynamic model.

The total electric potential $\Phi(R, t)$ is the sum of the external electric potential which satisfies the Poisson equation for the external charge density, $\nabla^2 \Phi_{\text{ext}}(R, t) = -4\pi \rho_{\text{ext}}(R, t)$, and the induced electric potential $\Phi_{\text{ind}}(R, t)$ due to polarization of the nanotubes valence electrons, satisfying $\nabla^2 \Phi_{\text{ind}}(R, t) = 4\pi n_1(r, t) \delta(r - a)$. These equations are easily solved by expressing the Coulomb interaction in cylindrical coordinates as usual,

$$\frac{1}{||R - R'||} = \sum_m \int \frac{dk}{(2\pi)^2} e^{i m \varphi} e^{i k z} g(r, r'; m, k)$$

(4)

where $g(r, r'; m, k) \equiv 4\pi I_m(|k| r_>) K_m(|k| r_<)$ is the radial Green’s function with $r_<=\min\{r, r'\}$, $r_>=\max\{r, r'\}$, and $I_m(x)$ and $K_m(x)$ being modified Bessel’s functions of the first and second kind, respectively. Finally, one can express the Fourier transform of the inverse dielectric function, $e^{-1}(R, R', t - t') = e^{-1}(r, r', \varphi - \varphi', z - z', t - t')$, as

$$\tilde{e}^{-1}(r, r'; m, k, \omega) = \frac{\delta(r - r')}{r'} - \delta(r' - a) g(r, a; m, k) \tilde{\chi}(m, k, \omega).$$

(5)

We consider a rigid distribution of external charges with density function $\tilde{\rho}_{\text{ext}}(R)$ which moves inside the nanotube at constant velocity parallel to its axis, $v = v e_z$, so that its density in the laboratory frame of reference can be written as $\rho_{\text{ext}}(R, t) \equiv \tilde{\rho}_{\text{ext}}(R - vt)$. Therefore, the Fourier transform of the external potential on the nanotube surface can be expressed as

$$\tilde{\Phi}_{\text{ext}}(a; m, k, \omega) = 2\pi \delta(\omega - kv) \int d^3R \tilde{\rho}_{\text{ext}}(R) f(R; m, k),$$

(6)

where we define $f(R; m, k) \equiv e^{-i(m \varphi + k z)} g(a; r; m, k)$. The factor $\delta(\omega - kv)$ indicates that the induced potential is stationary in the moving frame of reference attached to the external charge distribution. Denoting this potential by $\tilde{\Phi}_{\text{ind}}(R)$, we note that the induced potential in the laboratory frame is then $\Phi_{\text{ind}}(R, t) \equiv \tilde{\Phi}_{\text{ind}}(R - vt)$.

We further assume that the external charge density $\tilde{\rho}_{\text{ext}}(R)$ is both highly peaked and appreciable only around its center of mass at $R_0 = \{r_0, \varphi_0, z_0\}$ in the moving frame, giving rise to a well-defined multipole expansion, with total charge $Q = \int d^3R \tilde{\rho}_{\text{ext}}(R)$, and dipole moment $\mu = \int d^3R (R - R_0) \tilde{\rho}_{\text{ext}}(R)$. 


Figure 1. The torque (in meV/μ^2) on a point dipole with μ oriented in the plane passing through the dipole and the nanotube axis (so that φ = 0°), with θ being an angle relative to the direction of motion. The dipole is located at radial position \( r_0 \) (in Å) and is moving with speeds \( v = 3 \) and \( 5 \) parallel to the axis of a SWCNT of radius \( a = 7 \) Å. The contour step-size is \( Δτ = 0.2, 2, \) and \( 20 \) meV/μ^2 beginning at \( τ = 0.4, −2, \) and \( −20 \) meV/μ^2, respectively.
where we have used the Taylor expansion of \( f(\mathbf{R}; m, k) \) about \( \mathbf{R}_0 \), \( f(\mathbf{R}; m, k) \approx f(\mathbf{R}_0; m, k) + (\mathbf{R} - \mathbf{R}_0) \cdot \nabla_{\mathbf{R}_0} f(\mathbf{R}_0; m, k) \). Thus, the induced electric potential in the moving frame of reference can be written, for points \( \mathbf{R} \) in the neighborhood of the external charge, as

\[
\hat{\Phi}_{\text{ind}}(\mathbf{R}) \approx - \sum_m \int \frac{dka}{(2\pi)^2} f^*(\mathbf{R}; m, k) \hat{\chi}(m, k, \omega) \left[ Q f(\mathbf{R}_0; m, k) + \mathbf{\mu} \cdot \nabla_{\mathbf{R}_0} f(\mathbf{R}_0; m, k) \right],
\]

where, from now on, one has to set \( \omega = kv \) in \( \hat{\chi}(m, k, \omega) \). We evaluate the total electrostatic self energy, \( \mathcal{E}_{\text{self}} \), of the external charge distribution as

\[
\mathcal{E}_{\text{self}}(r_0) = \frac{1}{2} \int d^3 \mathbf{R} \hat{\rho}_{\text{ext}}(\mathbf{R}) \hat{\Phi}_{\text{ind}}(\mathbf{R}),
\]

Similarly, we obtain the dynamic polarization force, \( \mathbf{F}_{\text{ind}} \), on the external charge density as

\[
\mathbf{F}_{\text{ind}}(r_0) = \int d^3 \mathbf{R} \hat{\rho}_{\text{ext}}(\mathbf{R}) \hat{\mathbf{E}}_{\text{ind}}(\mathbf{R}) \approx Q \hat{\mathbf{E}}_{\text{ind}}(\mathbf{R}_0) + \mathbf{\mu} \cdot \nabla_{\mathbf{R}_0} \hat{\mathbf{E}}_{\text{ind}}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}_0},
\]

where \( \hat{\mathbf{E}}_{\text{ind}}(\mathbf{R}) = -\nabla_{\mathbf{R}} \hat{\Phi}_{\text{ind}}(\mathbf{R}) \) is the induced electric field in the moving frame of reference. We note that this force consists of a conservative part acting in the radial direction, \( -d\mathcal{E}_{\text{self}}(r_0)/dr_0 \), which corresponds to the classical dynamic image force on external charge distribution, and a dissipative part opposite to the direction of motion, with magnitude \( S = -\mathbf{e}_z \cdot \mathbf{F}_{\text{ind}} \), corresponding to the standard definition of stopping power.

Finally, the torque \( \mathbf{\tau} \) on the external charge distribution about its center of mass \( \mathbf{R}_0 \) in the moving frame may be evaluated as

\[
\mathbf{\tau}(r_0) = \int d^3 \mathbf{R} \hat{\rho}_{\text{ext}}(\mathbf{R}) (\mathbf{R} - \mathbf{R}_0) \times \hat{\mathbf{E}}_{\text{ind}}(\mathbf{R}) \approx \mathbf{\mu} \times \hat{\mathbf{E}}_{\text{ind}}(\mathbf{R}_0).
\]

As an illustration of the above model, we show the torque on a point dipole moving through a nanotube of radius \( a = 7 \) Å at a distance \( r_0 \) from its axis, with \( \mathbf{\mu} \) lying inside the plane which passes through the dipole and the nanotube axis (\( \phi = 0 \)), and having the direction \( \theta \) relative to the direction of dipole motion. Note that in this case, the torque has only the component perpendicular to the plane passing through the dipole and the nanotube axis, which is shown in Fig. 1 (per \( \mu^2 \)) versus \( r_0 \) and \( \theta \) for dipole speeds \( v = 0, 3 \) and \( 5 \) a.u. One notices surprisingly strong variations of the torque on a dipole with its speed, orientation and position inside carbon nanotube. One can assert that these effects are probably the result of an interplay between the image and stopping forces on a point dipole, and they may play important role in the self-alignment of polar molecules moving through constrained geometries [31].

### 3. Grazing scattering of slow ions from supported graphene

In the previous section we have studied the dynamic screening of fast ions and molecules due to the collective excitations of both \( \pi \) and \( \sigma \) electrons in carbon nanotubes, which can be conveniently described by the hydrodynamic model [30] for particle speeds above the so-called kinematic threshold for plasmon excitation being on the order of Bohr velocity, \( v_{\text{B}} \). Here, however, we are interested in slow ions, moving parallel to a graphene sheet at the speeds well under Bohr’s velocity, so that the dynamic response of graphene is dominated by the single-particle and collective excitations of its \( \pi \) electrons, whereas \( \sigma \) electrons are not excited owing to their having a large band gap. Such low-energy excitations require
going beyond the hydrodynamic model, and the dielectric-response theory for graphene, based on the random phase approximation (RPA) using linear approximation for the π electron bands [32, 33] is an adequate, if cumbersome way to proceed.

To make things simpler, we shall use here a semiclassical Vlasov equation for graphene’s π electrons in the relaxation-time approximation at finite temperatures, which should perform reasonably well when compared to the more complicated RPA dielectric formalism for extrinsic graphene, which is subject to a sufficiently high gate voltage, $V_g$ [34]. Since such graphene is characterized in equilibrium by a relatively large induced density per unit area of its π electrons, $n_g$ (typically, $|n_g| > 10^{12}$ cm$^{-2}$), the dynamic polarization of graphene is dominated by the intra-band electron excitations, which are reasonably well described by means of the Vlasov equation for slow ions moving at large distances from graphene. On the other hand, the relative simplicity of the semiclassical approach to dynamic screening in comparison to the RPA method permits an easy treatment of the finite gap between the graphene and a substrate (usually SiO$_2$), which will be found to exert quite strong influence on the dynamic-polarization forces on the incident ion.

We use a cartesian coordinate system with coordinates $R = \{r, z\}$, where $r = \{x, y\}$, and assume that graphene is placed in the $z = 0$ plane. A substrate with dielectric constant $\epsilon_{\text{sub}}$ ($\approx 3.9$ for SiO$_2$) is assumed to occupy the region $z \leq -h$ underneath the graphene, whereas the region $z > h$ is assumed to be vacuum or air. In the ground state of such system, the induced excess (or depleted) number density of the π electrons in graphene at temperature $T$ is given by

$$ n_g(\mu) = \frac{gd}{2\pi} \left( \frac{k_B T}{\hbar v_F} \right)^2 \left[ \text{dilog} \left( 1 + e^{-\mu/k_B T} \right) - \text{dilog} \left( 1 + e^{\mu/k_B T} \right) \right], \quad (12) $$

where dilation is the standard dilogarithm function, $gd = 4$ is the degeneracy factor and $v_F \approx c/300$ ($c$ being the speed of light) is the Fermi speed of graphene’s π-electron band in the approximation of linear energy dispersion, $\varepsilon_{\pm}(p) = \pm v_F p$, with $p$ being the electron quasi-momentum and $p$ its magnitude. Inverting the relation (12) can be used to deduce the value of chemical potential $\mu$ for any value of the externally applied gate voltage, $V_g$, by using the relation $n_g = \epsilon_{\text{sub}} \frac{V_g}{4\pi \hbar w_{\text{sub}}}$, where $w_{\text{sub}}$ is the thickness of the substrate (typically, $w_{\text{sub}} \gg h$).

When a point charge $Q$ moves parallel to graphene at a fixed distance $z_0 > 0$ above it with a constant velocity $\mathbf{v} = \{v_x, v_y\}$, so that its density can be written as $n_{\text{ext}}(r, z, t) = Q\delta(\mathbf{r} - \mathbf{v}t)\delta(z - z_0)$, then the resulting electric potential $\Phi_{\text{ext}}(r, z, t)$ will perturb the system giving rise to deviations from the ground-state charge densities (per unit area) on both the graphene and substrate surface, which we denote, respectively, by $\sigma_{\text{gr}}(r, t)$ and $\sigma_{\text{sub}}(r, t)$.

Next, we resort to the method of Doerr and Yu [35] to treat the effects of substrate on the response of graphene. The same method can be used to treat the effects of a cylindrical cavity in dielectric material on a carbon nanotube grown inside that cavity [30]. Denoting the electric potentials due to the induced charge densities $\sigma_{\text{gr}}$ and $\sigma_{\text{sub}}$, respectively, by $\Phi_{\text{gr}}(r, z, t)$ and $\Phi_{\text{sub}}(r, z, t)$, the total (screened) electric potential in the system, $\Phi$, can be written as the sum $\Phi = \Phi_{\text{gr}} + \Phi_{\text{ext}} + \Phi_{\text{sub}}$. Then, if there are no free charges on the substrate surface (such as, e.g., dopant centers), one can use the continuity of the normal component of the displacement vector,

$$ \left. \frac{\partial \Phi}{\partial z} \right|_{z=-h+0} = \epsilon_{\text{sub}} \left. \frac{\partial \Phi}{\partial z} \right|_{z=-h-0}, \quad (13) $$

to obtain $\sigma_{\text{sub}}$ [30, 34, 35]. This is easily implemented by using the Fourier transform (indicated by a tilde above transformed function) with respect to time, $t \to \omega$, and coordinates in the $xy$ plane, $r \to \mathbf{k}$, and by invoking the relation $\tilde{\sigma}_{\text{gr}}(\mathbf{k}, \omega) = -e \chi(\mathbf{k}, \omega) \hat{\Phi}(\mathbf{k}, z = 0, \omega)$ in terms of the polarization function of graphene, $\chi(\mathbf{k}, \omega)$. As a result, one obtains the Fourier transform of the induced potential at $z > 0$, $\tilde{\Phi}_{\text{ind}} = \tilde{\Phi}_{\text{sub}} + \tilde{\Phi}_{\text{gr}}$, as follows

$$ \tilde{\Phi}_{\text{ind}}(\mathbf{k}, z, \omega) = 2\pi Q\delta(\omega - \mathbf{k} \cdot \mathbf{v}) \frac{2\pi}{k} e^{-k(z+z_0)} \left[ \frac{1}{\epsilon(\mathbf{k}, \mathbf{k} \cdot \mathbf{v})} - 1 \right], \quad (14) $$
where \( \epsilon(k, \omega) = \epsilon_0(k) + \frac{2\pi i}{\hbar} \chi(k, \omega) \) is the dielectric function of the supported graphene, with

\[
\epsilon_0(k) \equiv \frac{\epsilon_{\text{sub}} + 1}{2} \left( 1 + \coth(kh) \right),
\]

being the background dielectric function which quantifies effects of the substrate on the response of graphene. We note that, while we assume \( \epsilon_{\text{sub}} \) to be constant, one can also include the effects of collective modes in the substrate due to, e.g., electron excitations in metallic substrates, or phonon excitations on the surface of an insulator, by assigning some frequency-dependent model to \( \epsilon_{\text{sub}} \).

To obtain the polarization function of graphene, \( \chi(k, \omega) \), one has to solve the linearized Vlasov-type equations for the probability density functions \( f_{\pm}(p, r, t) \) of graphene’s \( \pi \) electrons in the conduction (+) and valence (-) bands,

\[
\frac{\partial f_{\pm}}{\partial t} + v_{\pm}(p) \cdot \frac{\partial f_{\pm}}{\partial r} + e \frac{\partial}{\partial p} \Phi(r, z = 0, t) \cdot \frac{\partial f_{\pm}}{\partial p} = - \frac{f_{\pm} - f_{\pm}^0}{\tau(p)},
\]

where \( v_{\pm}(p) \equiv \partial \varepsilon_{\pm}(p)/\partial p = \pm v_F p/p \) is the electron velocity in the linearized \( \pi \) band, \( \Phi = \Phi_{\text{ext}} + \Phi_{\text{ind}} \) is the total potential, \( \tau(p) \) is the relaxation time due to collisions, and \( f_{\pm}^0 \equiv f(\varepsilon_{\pm}(p)) \) is the Fermi-Dirac distribution. As a result, one finds, in the collisionless limit, \( \tau \rightarrow \infty \),

\[
\epsilon(k, \omega) = \epsilon_0(k) + \frac{k_{\text{TF}}}{k} \left[ 1 - \left| \omega \right| \frac{H(\left| \omega \right| - k_F)}{\sqrt{\omega^2 - (k_F)^2}} + i \frac{\omega}{\sqrt{(k_F)^2 - \omega^2}} \right],
\]

where \( k_{\text{TF}} = 2\pi e^2 n_0(\mu) \), with \( n_0(\mu) \) from Eq. [12] is the Thomas-fermi inverse screening length, and \( H \) is the Heaviside step function. By using Eq. [17] in Eq. [14] one can evaluate the stopping and the image forces on the moving charge as follows: \( F_s = -\frac{2e}{\pi} v \cdot \frac{\partial}{\partial r} \Phi_{\text{ind}} \big|_{r = v t, z = z_0} \), \( F_i = -Q \frac{\partial}{\partial z} \Phi_{\text{ind}} \big|_{r = v t, z = z_0} \).

As an illustration of the above model, we show in Fig. 2 the velocity dependencies for the stopping and image forces on an ion moving at the distance \( z_0 = k_{\text{TF}}^{-1} \) parallel to the graphene in the collisionless limit of the dielectric function. Note that all the relevant quantities are defined in terms of the reduced units, where \( F_s \), \( F_i \) are \( (Q k_{\text{TF}})^2 \), \( \tau = v/v_F, \zeta_0 = z_0 k_{\text{TF}} \) and \( h = h k_{\text{TF}} \). One notices almost linear increase in the stopping force at low speeds due to the intra-band single-particle excitations of the \( \pi \) electrons, followed by a massive peak after the speed \( \tau = 1 \) which is a threshold for energy loss to the collective, or plasmon excitations, and a slow decrease in stopping force at the higher speeds. The image force shows similar resonant features around the speed \( \tau = 1 \) with the significant tendency of saturation at the lowest and the highest speeds shown. However, the most remarkable features shown in Fig. 1 are the very strong dependencies of both forces on the values of the graphene-substrate gap, with \( h = \infty \) standing for a free graphene, \( h = 0 \) being the zero-gap approximation usually employed in literature, whereas \( h = 0.5 \) is close to a realistic experimental value [36].

It is of particular interest to obtain analytical expressions for the image and stopping forces in the limit of vanishing projectile speed \( v \) describing slow charges moving over graphene. This can be achieved by assuming \( \gamma = 0 \) and \( \epsilon_0 = \) constant, so that one obtains a stopping force which is proportional to the ion speed, \( F_s = -\eta \overline{v} \), with the friction coefficient \( \eta \) given by

\[
\eta = \frac{1}{2 \epsilon_0} \left[ \frac{1}{\zeta} + 1 - (2 + \zeta) e^\zeta \operatorname{Ei}(1, \zeta) \right],
\]

and the static image force given by

\[
F_i = \frac{1}{\epsilon_0} \left[ \frac{1 - \epsilon_0}{\zeta^2} - \frac{1}{\zeta} + e^\zeta \operatorname{Ei}(1, \zeta) \right],
\]
Figure 2. The reduced (a) stopping and (b) image forces as functions of the reduced speed $\tau$ for an ion moving at the reduced distance $z_0 = 1$ above graphene for three values of the reduced gap between graphene and a SiO$_2$ substrate: $\bar{h} = 0.0$ (solid lines), 0.5 (dashed lines), and $\infty$ (dotted lines), with zero damping, $\tau = 0$.

where $\zeta \equiv 2z_0/\epsilon_0$ and $\text{Ei}(1, \zeta)$ is the standard exponential integral. Furthermore, one can easily obtain the leading terms in the asymptotic expansions when $\zeta \approx 4\frac{z_0^2}{v_B} \sqrt{\pi} g_0 |n_g| \to \infty$ in the above expressions for graphene in free space ($\epsilon_0 = 1$) which, physically, correspond to large distances $z_0$ and/or strongly gated graphene with a large equilibrium induced density of charge carriers $n_g$ at low temperatures. So, one obtains $F_i \sim -Q^2/(4z_0^2)$ for the image force, which is typical for a perfectly conducting surface and is consequently independent of $n_g$, whereas the low-speed stopping force becomes $F_s \sim -\frac{v_B}{v_B} \frac{Q^2}{16z_0^2} \frac{1}{\sqrt{\pi} g_0 |n_g|}$, which decreases as the inverse root of the density $|n_g|$. We note that, in the opposite limit of lightly gated, or intrinsic graphene (when $n_g \to 0$), the linear Vlasov theory for intra-band electron excitations becomes inadequate, as such processes are dominated by the inter-band electron transitions which are properly described by the RPA theory.

4. Concluding remarks

We have reviewed some aspects of modeling ion interactions with carbon nanotubes under channeling conditions and with graphene under grazing incidence, where dynamic polarization of carbon valence
electrons plays important roles. Specifically, we have evaluated the dynamic image force on ions and their energy loss to electron excitations. Such calculations were subsequently used to evaluate the role of those forces in the so-called Coulomb explosions of fast H\textsubscript{2} molecules in carbon nanotubes \cite{37}, as well as the effects of the dynamic image force on the so-called rainbow effect in angular distributions of fast protons channeled through short carbon nanotubes \cite{38}. By using hydrodynamic model for electron excitations, only plasmon excitations in carbon nanotubes were taken into account while calculating the ion stopping power, which should dominate at high ion speeds. While such mechanism of energy loss was found to have relatively small effect on ion channeling at high speeds \cite{38}, we have demonstrated here that the stopping force may play an important role in giving rise to a torque on a dipole which is channeled through a carbon nanotube. On the other hand, the image force on moving charges is adequately described by the hydrodynamic model, as shown in the recent discovery of electron image states around carbon nanotubes \cite{39}. Our exploration of the image force in channeling conditions has demonstrated that the torque on channeled dipoles, Coulomb explosion dynamics of molecules \cite{37}, and the rainbow peaks in proton channeling through carbon nanotubes \cite{38} are all strongly affected by the image force.

On the other hand, investigation of interactions of graphene with external particles is still in an early stage. We have, consequently, focused on interactions with slow ions, where peculiar band structure of graphene’s π electrons is expected to exhibit the most dramatic effects. While the linear-response treatment of such interactions involving intrinsic graphene is somewhat problematic, we have limited ourselves to the case of gated graphene, where kinetic-equation methods are expected to work well for electron excitations. We have found that both the single-electron, intra-band excitations and the collective plasmon excitations play important roles on the stopping and image forces. However, the most striking effect revealed in our calculations is due to the presence of a gap between the graphene and a polarizable substrate. Surprisingly, all theoretical models of graphene’s dynamic response assume a zero gap \cite{32,33}, so we point to a strong need to take into account the finite size of such a gap, which can reach values of ∼ 4.2 Å, as documented experimentally \cite{36}.

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