

LINEAR AND NONLINEAR DYNAMIC CONDUCTIVITY OF CARBON NANOTUBES

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Electronic properties of carbon nanotubes are studied. Linear response of dynamic conductivity of both zigzag and armchair nanotubes is analyzed at different temperatures and for different radii of nanotubes in the framework of semiclassical theory. Simplified approach is used by introducing the momentum independent relaxation time approximation. At the second stage, the nonlinear response of semiconducting zigzag carbon nanotubes is studied within the same framework. It is found that the third order response of dynamic conductivity diverges logarithmically with the increase in the radius of Carbon Nanotube. Analytic proof of this result is presented. The validity of the application of semiclassical theory for studying the nonlinear electronic properties of carbon nanotubes is discussed.

Keywords: Carbon Nanotubes, Nanophysics, Graphene, Nonlinear conductivity.

I. INTRODUCTION

It all begins with Fullerenes. Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before. Therefore, fullerenes in general form an interesting class of compounds that surely will be used in future technologies and applications. Before the first synthesis and detection of the smaller fullerenes C_{60} and C_{70} , it was generally accepted that these large spherical molecules were unstable. However, Bochvar et al. and Stankevich et al. [1, 2], already had calculated that C_{60} in the gas phase was stable and had a relatively large band gap. The most attractive feature of fullerene is that its crystalline structure depends on the conditions of its preparation, with different structures possessing quite different physical response.

As is the case with numerous, important scientific discoveries, fullerenes were accidentally discovered. In 1985, Kroto and Smalley [3] found strange results in mass spectra of evaporated carbon samples. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started.

Carbon Nanotubes (CNs) can be described as the material lying between fullerenes and graphite as a new member of Carbon allotropes. Discovered in 1991 by Sumio Iijima [4], CNs have drawn a lot of attention because of their unusual physical properties. They are made of a highly ordered sheet of carbon atoms rolled into a tube. They are known to have exceptional mechanical exibility and strength [6, 7].

The nanotubular fullerenes are generally called carbon nanotubes(CNs). A CN is a fullerene rolled up into a 20-100 Å diameter cylinder weight ratios which makes them attractive mechanically [14], but they also have interesting electromagnetic properties.

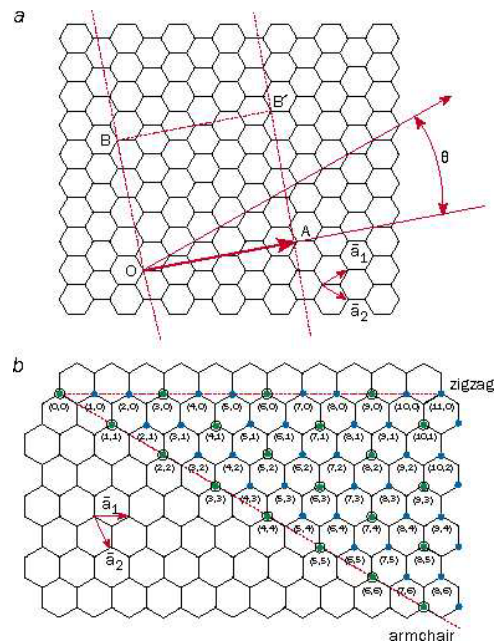


Figure 1: (a) Vector OA is called the chiral vector. It can be defined by the vector $C_h = na_1 + ma_2$ and the chiral angle with the zigzag axis. Vectors a_1 and a_2 are the lattice vectors. (b) All possible structures of SWNTs can be formed from chiral vectors lying in the range given by this figure. (n,m) with n,m integer and $m \cdot n$ or $\mu < 30^\circ$ [6, 7].

CNs can exhibit electrical conductivity similar to that of copper, thermal conductivity as high as diamond and can exhibit mechanical strength greater than steel. Because carbon is the basis of most materials we use everyday, CNs are expected to be easily manipulated using the versatile chemistry of carbon. They come in two forms Single Walled Carbon Nanotubes (SWCN) and Multi-Walled Carbon Nanotubes (MWCN). The SWCNs have a tubular form with a diameter as small as 1 nm and a length a few nm to microns long. They are con gurationally equivalent to a two dimensional graphene sheet rolled in a tube. CNs can also be metallic or semi-conducting depending on the chirality. Experiments verified this prediction [9].

Properties of electrons in nanotubes and electron transfer processes in them have been greatly studied both theoretically and experimentally. The theoretical

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analysis is often confined to dynamics of π -electrons within the approximation of tight-binding [10, 11], which allows for hopping between only three adjacent atoms of the hexagonal structure.

In some previous works [16, 17], linear electromagnetic response properties of a single CN are modeled through effective boundary conditions. That model is widely applied in microwave electronics and antenna theory, e.g., for the design of semi-transparent screens and helical sheaths in traveling wave tubes [19]. It entails the replacement of a real nanotube by a continuous, infinitely thin, cylindrical surface on which two-sided impedance boundary conditions for the electromagnetic field are laid down. The surface impedance tensor is expressed in terms of the dynamic conductivity of nanotube.

There have been done several works [20–22] on nonlinear properties (optical and electrical) of CNs where scientists tried to develop efficient theories of nonlinear susceptibility and conductivity [25]. There are considerable interest on the nonlinear properties of both semiconductor and metallic CNs. In case of semiconductor CNs nonlinear properties are important not only because the nonlinear spectrum gives information on their electronic structure, but also in view of the possible device applications. The promising features of CNs for use of in the nonlinear optical devices include the fact that at frequencies greater than infrared frequencies of the lattice vibration, the main contribution to the optical nonlinearities comes from the 1D motion of delocalized π -band electrons at a fixed lattice ion configuration. By virtue of this circumstance one can expect that semiconductor CNs will have fast, electronic, nonlinear response and the large, non-resonant, third-order optical susceptibility. In its turn, this last feature can lead to a combination of a large nonlinear refractive index with relatively low optical losses which is of a considerable importance to get a high performance of nonlinear optical devices. Moreover, the band gap for a semiconductor tubule is inversely proportional to tubule diameter [5, 15], so that we have the possibility of designing new materials with desired nonlinear-optical response characteristics which can be essential for practical application.

Nonlinear electron transport effects in chiral nanotubes has been studied in ref. [22]. In that work, spiral model has been used to develop a general analytic theory of electronic theory in a CN. A simplified model is given in the framework of semiclassical theory. It is assumed that a CN is exposed to ac and dc fields, and nonlinear contribution of the ac electric field to the magnitude and the direction of the total time averaged current is estimated. In that picture, it is assumed that electrons in a CN moves only in the direction parallel to the axis and along the direction geometric chiral angle, θ . This model gives appreciably good results for certain cases but it does not describe the generic nonlinear behavior of CNs, e.g. it can't describe the nonlinear behavior of zigzag and armchair CNs.

The main goal of this work is to study the nonlinear response of dynamic conductivity of carbon nanotube with external field. To study the nonlinear conductivity

of CNs we have taken the following key points,

- Transverse quantization of electron momentum inside CN.
- Semiclassical approximation.
- Momentum independent relaxation time approximation in Boltzmann kinetic equation.
- No inter band transition, i.e. no transition between different s -states.

We have investigated the applicability of semiclassical approx. in case of non-linear response of semiconducting CNs. We have not investigated Chiral nanotubes, and therefore, restricted ourselves within Zigzag and Armchair nanotubes.

In the first part of our work we have reviewed the *linear response* of current density of CNs to the external electric field. We have investigated the dependence of conductance with CN geometry. We have worked on zigzag CNs (both semiconducting and metallic), and on armchair CNs.

In the second part, we have studied the *nonlinear response* of current density of CNs to the external field. We have also studied the geometric dependence of CN's non-linear conductivity. To study the nonlinear response, we have extracted the coefficient of third order term, $\sigma^{(3)}$, as a function of radius from the non-equilibrium distribution function by Taylor expansion. We have investigated its characteristic behavior.

II. THEORY

Dispersion Properties

Before describing the dispersion properties of π -electrons we would like to know the relation between the physical radius of CN and the chiral vector. We know the geometric chiral vector is represented by

$$\mathbf{C}_h(n, m) = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (1)$$

where \mathbf{a}_1 and \mathbf{a}_2 are lattice vectors, and m and n are chiral lattice vector (integer) indices. The physical radius of CN is related to these indices as,

$$R_{cn} = \frac{\sqrt{3}b}{2\pi} \sqrt{m^2 + mn + n^2}, \quad \tan \theta_{cn} = \frac{\sqrt{3}n}{2m + n} \quad (2)$$

where $b = 0.142$ nano meters is the distance between adjacent atoms in the elementary graphene cell and θ_{cn} is called the geometric chiral angle.

A Carbon Nanotube is just a special form of graphene sheet. As we have mentioned earlier, CN's are made from planar graphene sheets where graphene sheets are rolled to form tubes of very small diameter. When graphene sheet is rolled to form CN the transverse motion of electron becomes quantized because of the periodic boundary condition of the tubular graphene sheet. The dispersion relation of the

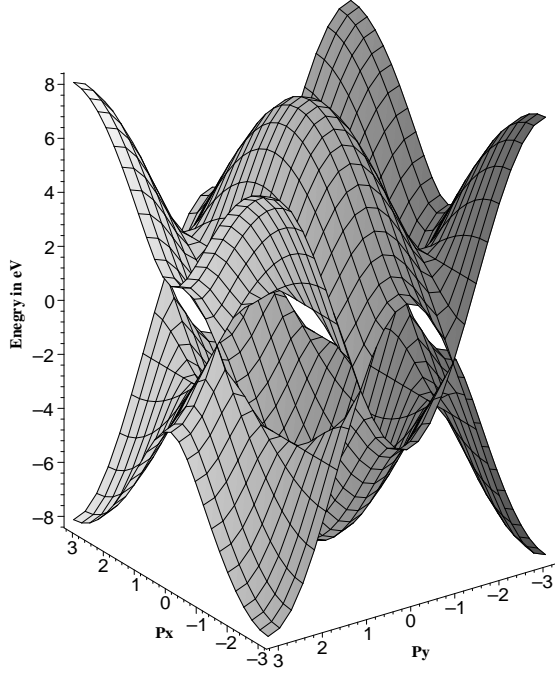


Figure 2: Dispersion relation of planar graphite sheet , here p_x and p_y are dimensionless quantity in the 1st Brillouin zone.

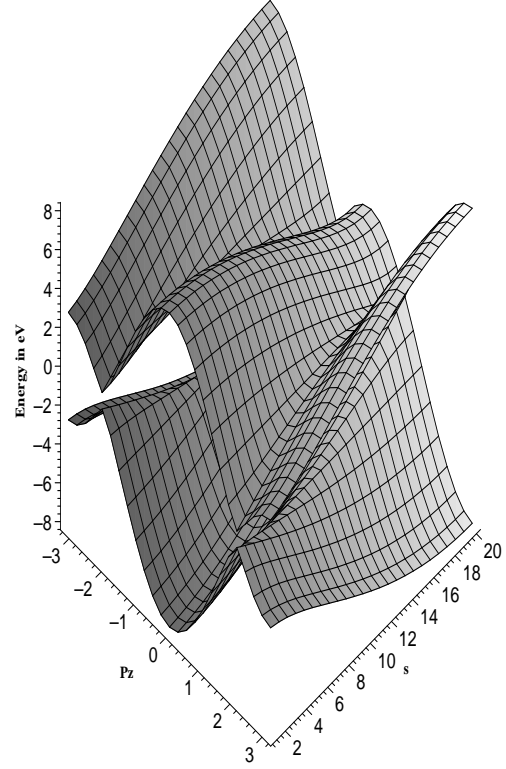


Figure 4: Dispersion relation of Armchair CN for $m=20$. Note that there always remains two minima for all values of s . There are two Fermi points in the first Brillouin zone.

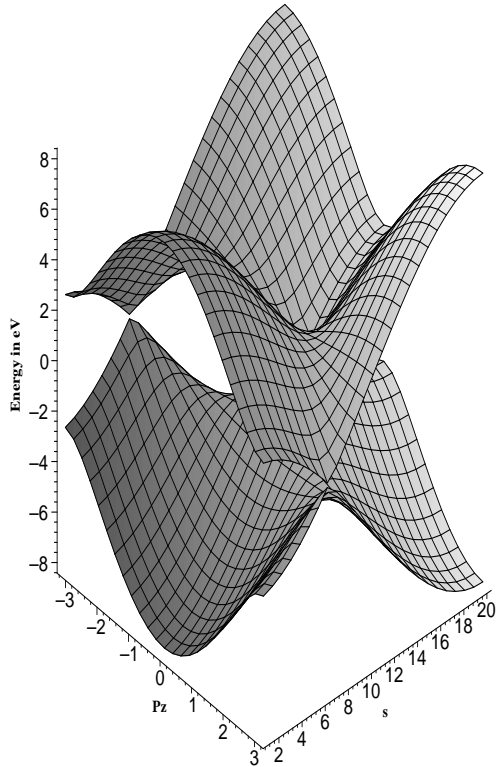


Figure 3: Dispersion relation of Zigzag CN for $m=20$. Note the change in minima due to change in value of s . We see presence of one or two minima depending on value of s . There are three Fermi points in the first Brillouin zone.

graphene sheet with hexagonal lattice is given by [10, 11, 13, 18] Equ.3.

Here, the overlap integral $\gamma_0 = 2.7$ eV for carbon, and $b = 1.42$ is the interatomic distance in a graphite sheet. the positive and negative signs in Eq.(3) correspond to the conduction and the valence bands, respectively. The range of the quasimomentum \mathbf{p} is confined within the hexagonal first Brillouin zone.

A fundamental distinction between CN and graphene is in the transverse quantization of charge-carrier motion [10, 11], which causes p_x and p_y to exhibit discrete spectra. Zigzag CNs are classified by the dual index $(m, n = 0)$ [4, 6]. From Eq.(3), we observe that the x and y directions in Eq.(3) correspond to the z and ϕ directions. After substitution $\{p_x \rightarrow p_z, p_y \rightarrow p_\phi\}$ we have p_ϕ quantized as follows,

$$p_\phi = \frac{2\pi\hbar s}{\sqrt{3}mb}, \quad s = 1, 2, \dots, m \quad (4)$$

The electron dispersion relation for zigzag CNs thus takes the form of equation 5

$$\xi(p_z, s) = \pm\gamma_0 \sqrt{1 + 4 \cos\left(\frac{3bp_z}{2\hbar}\right) \cos\left(\frac{\pi s}{m}\right) + 4 \cos^2\left(\frac{\pi s}{m}\right)} \quad (5)$$

In case of armchair nanotubes, which are classified by dual index $(m, n = m)$, we have to substitute $\{p_x \rightarrow p_\phi, p_y \rightarrow p_z\}$ where p_ϕ has the discrete values as,

$$p_\phi = \frac{2\pi\hbar s}{3mb}, s = 1, 2, \dots, m \quad (6)$$

Therefore, the dispersion relation for armchair nanotube becomes Eq. 10.

Dynamic Conductivity of a Carbon Nanotube

To deal with the CNs we would like to apply semiclassical approximation to describe the motion of π -electrons exposed to the electromagnetic field of a transversely symmetric (i.e., $\frac{\partial}{\partial\phi} \equiv 0$) surface wave in a single-shell CN. We start with the Boltzmann kinetic equation

$$\frac{\partial f}{\partial t} + eE_z \frac{\partial f}{\partial p_z} + v_z \frac{\partial f}{\partial z} = J[F(\mathbf{p}); f(\mathbf{p}, z, t)] \quad (7)$$

where \mathbf{p} is the electron's two-dimensional quasimomentum tangential to the CN's surface, p_z is the pro-

jection of \mathbf{p} on the axis of the CN, $v_z = \frac{\partial\xi}{\partial p_z}$ is the electron velocity, $\xi = \xi(\mathbf{p})$ is the energy dispersion relation with respect to the Fermi level, and $J(F; f)$ is the collision integral. The chemical potential of graphite being null-valued [10], the Fermi equilibrium distribution function

$$F(\mathbf{p}) = \frac{1}{1 + \exp\left\{\frac{\xi(\mathbf{p})}{k_B T}\right\}} \quad (8)$$

involves only the Boltzmann constant k_B and the temperature T . In the so-called momentum-independent relaxation time approximation [12], the collision integral is given by,

$$J[F(\mathbf{p}); f(\mathbf{p}, z, t)] = \nu[F(\mathbf{p}) - f(\mathbf{p}, z, t)] \quad (9)$$

where ν is the relaxation frequency. For simplicity ν is assumed to be constant and equal to the reciprocal of the time of electron mean-free path. Numerical estimation of $1/\nu$ for armchair nanotubes can be found in the ref. [23].

For the simplicity of our calculation, we will neglect the effect of spatial non-locality by assuming that the wavelength of the applied electric field is large compared to nanotube length scale. Therefore, we can neglect the spatial variation of f . So, we can write $\frac{\partial f}{\partial z} = 0$. Therefore, Solution of Eq. 7 can be written as Eq. 11.

$$\xi(p_z, s) = \pm\gamma_0 \sqrt{1 + 4 \cos\left(\frac{\pi s}{m}\right) \cos\left(\frac{\sqrt{3}bp_z}{2\hbar}\right) + 4 \cos^2\left(\frac{\sqrt{3}bp_z}{2\hbar}\right)} \quad (10)$$

$$f(p_z, t) = \mathbf{e}^{(-\nu t)} \int^t \nu F \left(e \int E_{t'}(t') dt' + p_z - e \int E_z(t) dt \right) \mathbf{e}^{(-\nu t')} dt' + C \mathbf{e}^{-\nu t} (p_z - e \int E_z(t) dt) \quad (11)$$

where C is a constant of integration. We assume that $\nu \gg t$, so the second term is negligible. Therefore,

we have,

$$f(p_z, t) = \mathbf{e}^{(-\nu t)} \int^t \nu F \left(e \int E_z(t') dt' + p_z - e \int E_z(t) dt \right) \mathbf{e}^{(-\nu t')} dt' \quad (12)$$

We take the external electric field to be of the form $E_z = \Re[E_z^0 e^{i(kz - \omega t)}]$, where k is the axial wave number and ω is the angular frequency of the EM field. Since, we have neglected spatial non-locality we set below, $k = 0$. Now expanding $f(p, z, t)$ in power of

$E_z(t)$, we can write $f = F + \Re[\delta f e^{-i\omega t}]$ with δf containing the terms of higher orders in $E_z(t)$. Keeping only the linear terms in E_z^0 , we can write,

III. RESULTS

$$\delta f^{(1)} = -i \frac{\partial F}{\partial p_z} \frac{eE_z^0}{\omega + i\nu} \quad (13)$$

Taking the 3^{rd} order term into account we have,

$$\delta f^{(3)} = i \frac{\partial^3 F}{\partial p_z^3} \frac{e^3 E_z^0{}^3}{(\omega + i\nu)^3} \quad (14)$$

The axial surface current density $J_z = \Re[J_z^0 e^{i(kz - \omega t)}]$ is determined by the relation,

$$J_z = \frac{2e}{(2\pi\hbar)^2} \iint_{1^{st} BZ} v_z f d^2\mathbf{p} \quad (15)$$

where e is the electron charge and the integration is over the first Brillouin Zone (1st BZ). Eq. (13) contributes to the linear response of the current density to the external electric field and Eq. (14) contributes to the nonlinear response. The second order term of f does not contribute to the current density J_z because of inversion symmetry of CN geometry. The relation between J_z and E_z^0 can be written as,

$$J_z^{(1)} = \tilde{\sigma}_{zz}^{(1)}(\omega) E_z^0 \quad (16)$$

and for the nonlinear response,

$$J_z^{(3)} = \tilde{\sigma}_{zz}^{(3)}(\omega) E_z^0{}^3 \quad (17)$$

therefore the first and third order axial conductivity can be written as,

$$\tilde{\sigma}_{zz}^{(1)}(\omega) = -i \frac{2e^2}{(2\pi\hbar)^2} \frac{1}{(\omega + i\nu)} \iint_{1^{st} BZ} \frac{\partial F(\mathbf{p})}{\partial p_z} v_z(\mathbf{p}) d^2\mathbf{p} \quad (18)$$

and,

$$\tilde{\sigma}_{zz}^{(3)}(\omega) = i \frac{2e^4}{(2\pi\hbar)^2} \frac{1}{(\omega + i\nu)^3} \iint_{1^{st} BZ} \frac{\partial^3 F(\mathbf{p})}{\partial p_z^3} v_z(\mathbf{p}) d^2\mathbf{p} \quad (19)$$

respectively.

Eq.(18) and (19) can be applied to zigzag and armchair CN's to study their both linear and nonlinear responses to the external field.

Because of discrete behavior of the transverse motion of electrons in CNs the expression for conductivity(Eq.18 & 19) changes as,

$$\tilde{\sigma}_{zz}^{(1)}(\omega) = -\frac{2iw_{cn}e^2}{3\pi\hbar mb} \frac{1}{\omega + i\nu} \sum_{s=1}^m \int_{-p_0}^{p_0} v_z(p_z, s) \frac{\partial F}{\partial p_z} dp_z \quad (20)$$

and

$$\tilde{\sigma}_{zz}^{(3)}(\omega) = \frac{2iw_{cn}e^4}{3\pi\hbar mb} \frac{1}{(\omega + i\nu)^3} \sum_{s=1}^m \int_{-p_0}^{p_0} v_z(p_z, s) \frac{\partial^3 F}{\partial p_z^3} dp_z \quad (21)$$

where $p_0 = 2\pi\hbar/(\sqrt{3}w_{cn}b)$ and $w_{cn} = 1$ corresponds to the armchair nanotubes and $w_{cn} = \sqrt{3}$, to zigzag nanotubes.

Linear response

The linear conductivity of both zigzag and armchair CNs are studied as a function of temperature and radius of the CN. It is known that zigzag CN shows both metallic and semiconducting behavior depending on the chiral angle. From Fig. 5 it is seen that for semiconducting zigzag CN ($m \neq 3q$) linear conductivity increases with m (therefore, radius) and it is approaching asymptotic value of that of graphene plane. The temperature dependence also reflects that physical property of a semiconductor. Higher temperature is causing higher conductivity. The upper branch of Fig. 5 shows the temperature and radius dependence of metallic zigzag CNs ($m = 3q$). Conductivity decreases with increase in m (or radius) which shows that metallic property of CN approaches to semimetallic property of graphene plane for large radius. And also higher temperature causes lower conductivity which reflects metallic property.

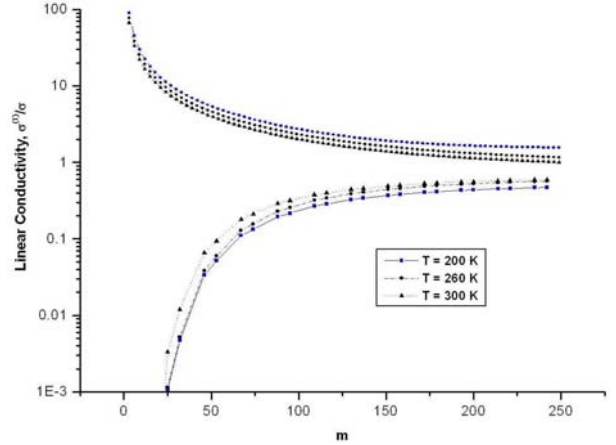


Figure 5: Scaled linear conductivity vs m graph of Zigzag CN. Zigzag CN can be either semiconductor ($m \neq 3q$) or metal ($m = 3q$). The temperature dependence of conductivity supports both semiconducting and metallic behavior of zigzag CN. Here, $\sigma \equiv \sigma_{\infty}$.

Linear property of armchair CN is presented as seen in Fig. 6. It also shows metallic property. Larger radius of armchair causes $\sigma^{(1)}$ to approach the semimetallic property of graphene plane.

Analytic study of the asymptotic property of the linear term

The integral in Eq.(20) can be analytically estimated asymptotically with respect to the large parameter $\lambda = \gamma_0/k_B T$ taking into account that the Fermi points provide the main contribution to these integrals. Following the work of Wallace [18], in the vicinity of Fermi points we can apply the approximate that the dispersion relation is linear and can be written as,

$$\xi(\mathbf{p}) \simeq \pm \frac{3\gamma_0 b}{2\hbar} |\mathbf{p} - \mathbf{p}_F| \quad (22)$$

where \mathbf{p}_F is the constant quasimomentum corresponding to particular Fermi point.

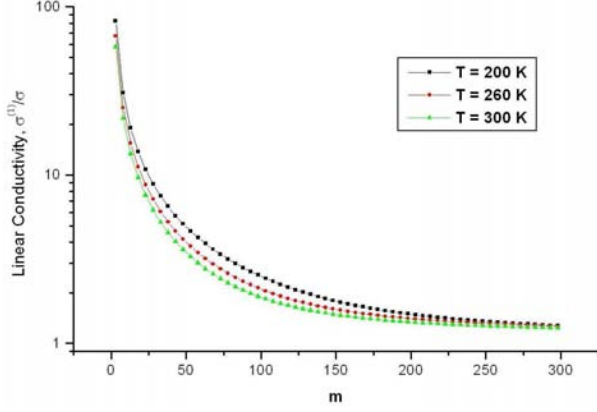


Figure 6: Scaled linear conductivity, $\sigma^{(1)}$ vs m graph of Armchair CN. Armchair CN are metallic. It is obvious from the temperature dependence of the conductivity as Armchair CN shows lower conductivity at higher temperature. Here, $\sigma \equiv \sigma_\infty$.

We transform the integration over \mathbf{p} to the integration over ξ and ϕ . Changing the cartesian coordinate (p_x, p_y) to polar coordinate (ξ, ϕ) by taking $\left(\frac{3\gamma_0 b}{2\hbar}\right)(p_x - p_{F_x}) = \xi \sin \phi$ and $\left(\frac{3\gamma_0 b}{2\hbar}\right)(p_y - p_{F_y}) = \xi \cos \phi$, we can write $d^2\mathbf{p} = \left(\frac{2\hbar}{3b\gamma_0}\right)^2 \xi d\xi d\phi$ as per Wallace [18]. Extending the integration over $0 \leq \xi < \infty$ and $0 \leq \phi \leq 2\pi$ we find,

$$\begin{aligned} \iint_{1^{st} BZ} v_z^2 \frac{\partial F}{\partial \xi} d^2\mathbf{p} &\cong \\ -\frac{1}{2k_B T} \int_0^\infty \frac{\xi d\xi}{\cosh^2\left(\frac{\xi}{2k_B T}\right)} \int_0^{2\pi} \sin^2 \phi d\phi & \\ = -2\pi k_B T \ln 2 &\quad (23) \end{aligned}$$

Using this result in Eq.(18) we find,

$$\sigma^{(1)} \simeq i \frac{2 \ln 2}{\pi \hbar^2} \left(\frac{e^2 k_B T}{\omega + i\nu} \right) \quad (24)$$

The asymptotic value of Eq.(20) approaches the above estimated value in the limit $m \rightarrow \infty$.

Nonlinear response

We have studied the nonlinear conductivity of the both semiconducting and metallic zigzag CNs. We have explained the results of our works in the following sections.

Semiconducting Zigzag CNs

The result of the numerical works is been shown in Fig. 7 & 8. In case of semiconducting CN, for low value of m it is seen that the conductivity increases with the increase in value of m which is what we would physically expect. For large m the CN behaves as semimetallic graphene sheet. From the temperature dependence it is seen that at low temperature nonlinear conductivity, $\sigma^{(3)}$ is lower than that of at high temperature. The change in property from semiconductor to semimetal occurs above m around 250. The

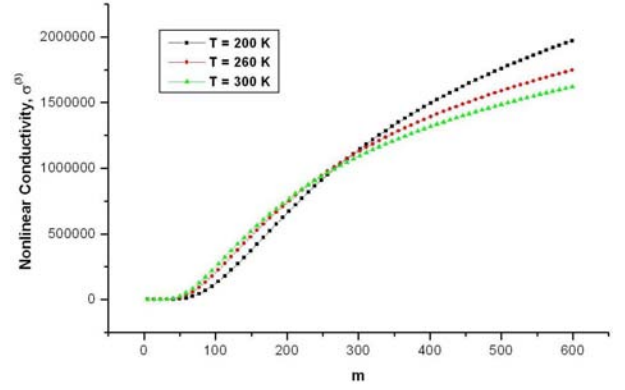


Figure 7: Nonlinear conductivity $\sigma^{(3)}$ of semiconducting zigzag nanotubes at different temperatures. Here, $\sigma^{(3)}$ is proportional to $\left(\frac{2e^4}{\sqrt{3}\pi\hbar b (\sqrt{\omega^2 + \nu^2})^3} \right)$.

unsatisfactory part of this result is that $\sigma^{(3)}$ does not converge with the increase in m . In following section we will show that $\sigma^{(3)}$ is a logarithmically diverging function of m . Therefore, the result is not physical. Semiclassical theory can still be applied to study $\sigma^{(3)}$ for CN with small radius. There must be a cutoff value of m , say m_c , up to which semiclassical theory can be applied without problem. From Fig. 7 & 8 we can estimate $m_c \approx 250$.

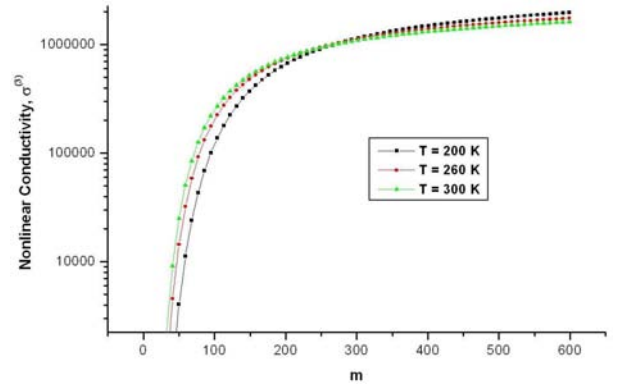


Figure 8: Log scaled variation of nonlinear conductivity $\sigma^{(3)}$ of semiconducting zigzag nanotubes with m at different temperatures. Here, $\sigma^{(3)}$ is proportional to $\left(\frac{2e^4}{\sqrt{3}\pi\hbar b (\sqrt{\omega^2 + \nu^2})^3} \right)$.

Presence of singularity in the third order term

The third order term, $f^{(3)}(p_z, m, s, T)$, of the non-equilibrium distribution function $f(p_z, m, s, T)$ shows strange behavior in cases of both Zigzag and Armchair CNs. We have found out the $f^{(3)}(p_z, m, s, t)$ cannot be integrated over \mathbf{p} at certain parameter values. It is found that for zigzag metallic case ($m = 3q$), $f^{(3)}$ has singularity at $p_z = 0$ and $p_z = \pi$ for $s/m = 1/3$ and $s/m = 2/3$, respectively. Close to the singular point p_0 , we can write,

$$f^{(3)} \propto \frac{1}{|p_z - p_0|^\alpha} \quad (25)$$

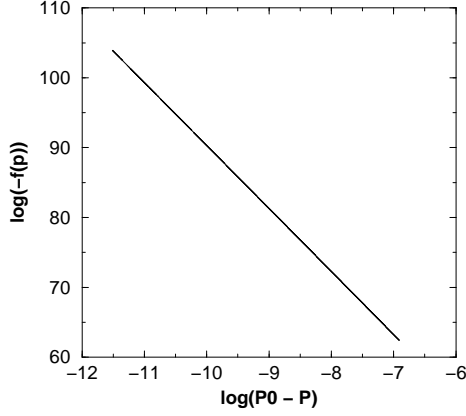


Figure 9: Zigzag Metallic CN. Determination of the value of α close to singular point $p_z = \pi$ for parameter ratio $s/m = 1/3$. It is found that $\alpha \approx 8.98$. Hence, the function is non integrable in $p_z = [-\pi, \pi]$

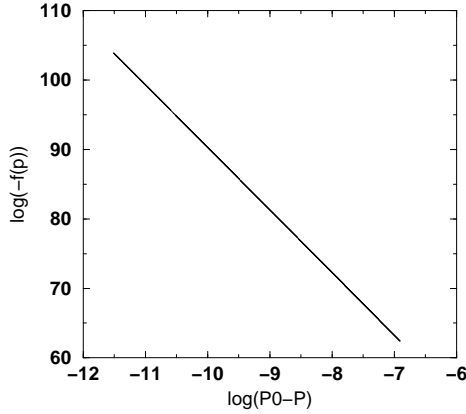


Figure 10: Zigzag Metallic CN. Determination of the value of α close to singular point $p_z = 0$ for parameter ratio $s/m = 2/3$. Here we have $\alpha \approx 8.995$. Also non integrable in $p_z = [-\pi, \pi]$

It is found that in case of armchair CN $f^{(3)}(p_z, m, s, T)$ has singularity at $p_z = \frac{\pi}{3}$ for parameter values $s/m = 1$. To determine the integrability of $f^{(3)}$ we have used the approach of Eq.(25) For zigzag CN ,Fig. 9, we see the value of $\alpha \approx 8.98$ for $s/m = 1/3$ and $p_z = \pi$. In case of the ratio $s/m = 2/3$ we find $f^{(3)}$ has singularity at $p_z = 0$. From Fig. 10, we found $\alpha \approx 8.995$. For armchair CN, Fig. 11 we found $\alpha \approx 10.8$. Therefore, in case metallic CN, at certain parameter values of (m, s)

Analytic study of Nonlinear conductivity of CN with large radius

In order to calculate the nonlinear conductivity we have to perform the integration of Eq.(19) over 1st Brillouin Zone. To simplify our calculation we perform the integration in polar coordinate where we write $d^2\mathbf{p} = \left(\frac{2\hbar}{3b\gamma_0}\right)^2 \xi d\xi d\phi$ and we write $\frac{\partial^3 F(\mathbf{p})}{\partial p_z^3}$ as,

$$\frac{d^3 F}{dp_z^3} = v_z'' \frac{\partial F}{\partial \xi} + 3v_z v_z' \frac{\partial^2 F}{\partial \xi^2} + v_z^3 \frac{\partial^3 F}{\partial \xi^3} \quad (26)$$

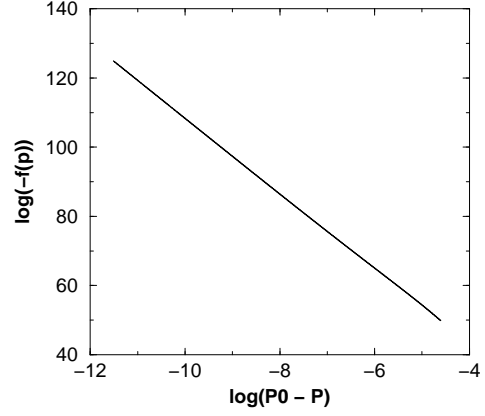


Figure 11: Armchair CN. Determination of the value of α close to singular point $p_z = \frac{\pi}{3}$ for parameter values $s/m = 1$. We have $\alpha \approx 10.8$. Therefore the function is non integrable in $p_z = [-\pi, \pi]$.

so we have to perform the integration,

$$\int_0^\infty \int_0^{2\pi} v_z \left(v_z'' \frac{\partial F}{\partial \xi} + 3v_z v_z' \frac{\partial^2 F}{\partial \xi^2} + v_z^3 \frac{\partial^3 F}{\partial \xi^3} \right) \xi d\xi d\phi \quad (27)$$

where $v_z = \frac{\partial F}{\partial p_z}$ and v_z' and v_z'' are derivatives w.r.t. p_z .

$$v_z = -2 \frac{\gamma_0 \sin(a_0 p_x) a_0 \cos(b_0 p_y)}{\sqrt{1 + 4 \cos(a_0 p_x) \cos(b_0 p_y) + 4 (\cos(b_0 p_y))^2}}$$

$$v_z = -2 \frac{\gamma_0^2 \sin(a_0 p_x) a_0 \cos(b_0 p_y)}{\xi}$$

and v_z' and v_z'' are calculated in the similar way. Here, $a_0 = \frac{3b}{2\hbar}$ and $b_0 = \frac{\sqrt{3}b}{2\hbar}$. Performing Taylor expansion of v_z, v_z' and v_z'' about any one of the Fermi points $(p_{F_x}, p_{F_y}) \equiv (0, \frac{2\pi}{3b_0})$ or $(p_{F_x}, p_{F_y}) \equiv (\frac{\pi}{a_0}, \frac{\pi}{3b_0})$ and substituting $\gamma_0^2 a_0^2 (p_x - p_{F_x}) \rightarrow \xi \sin(\phi)$ and $\sqrt{3} \gamma_0^2 a_0 b_0 (p_y - p_{F_y}) \rightarrow \xi \cos(\phi)$ and keeping only the leading terms, we have,

$$v_z = \sin(\phi) \quad (28)$$

$$v_z' = \frac{\cos^2(\phi)}{\xi} \quad (29)$$

and

$$v_z'' = -3 \frac{\sin(\phi) \cos^2(\phi)}{\xi^2} \quad (30)$$

the last two terms of right hand side in Eq.(26) can be integrated when placed in Eq.(27). Only first term

causes divergence at $\xi \rightarrow 0$, since

$$\xi v_z v_z'' \frac{\partial F}{\partial \xi} \propto \frac{1}{\xi \cosh^2(\xi/2)} \quad (31)$$

Therefore, the first term gives logarithmically divergent result when integrated over the range $\xi = [0, \infty]$. Therefore, using this simplified semiclassical model it is not possible to calculate the third order response of the electrical conductivity at large m . Since, for $m \rightarrow \infty$, $\sigma^{(3)}$ of CN must coincide with that of planar graphene, CN's $\sigma^{(3)}$ also diverges logarithmically with increasing m .

IV. CONCLUSION

To summarize, we have studied the linear and nonlinear responses of electrical conductivity of Carbon nanotube in the framework of semiclassical theory. Carbon nanotube has a complicated electronic structure. In order to overcome mathematical complexity we have introduced the momentum independent relaxation time approximation in the classical Boltzmann kinetic equation. This approximation simplifies mathematical complexity at the price of some system information, e.g. energy dependence of the relaxation time, electron-phonon interaction etc. We have analyzed the linear response of dynamic conductivity of both zigzag and armchair nanotubes using semiclassical theory at different temperature. The results that we have obtained in case of linear response is compatible with experimental findings.

Our aim was to study the nonlinear response of dynamic conductivity of CNs. Since, Semiclassical theory is proved to be valid in case of linear conductiv-

ity of CNs, the nonlinear response of Zigzag semiconductor nanotube is also studied in the same framework. It is observed that in this framework the nonlinear conductivity, $\sigma^{(3)}$, gives physical result only up to certain value of CN radius. Above that certain radius $\sigma^{(3)}$ diverges logarithmically as function of m (or radius, R_{cn}).

It is found that there are presence of non-integrable singularities in $f^{(3)}$ when integrated over the 1st Brillouin zone. The first and second order terms, $f^{(1)}$ & $f^{(2)}$ respectively, do not show any discontinuity in the domain of 1st Brillouin zone. Both metallic and semiconducting diverges with the increase in m . It is shown both analytically and numerically. In this work we have demonstrated that semiclassical theory with relaxation time approximation is not appropriate for describing the nonlinear response of dynamic conductivity of CNs at arbitrary R_{cn} .

Further study is required to overcome this problem. In our calculation we have neglected the transition between different s -states. Also, we have replaced the collision integral with the simplified relaxation frequency. We propose further investigation with the inclusion of above points. Relaxation frequency can be a function of energy and this energy term could also cancel the diverging term in the integral (Eq.27).

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