Negative Differential Conductivity in Carbon Nanotubes

Anton S. Maksimenko and Gregory Ya. Slepyan
Institute for Nuclear Problems, Belarus State University, Bobruiskaya strasse 11, Minsk, 220050, Belarus
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A theoretical model and computations of the I-V characteristics of long carbon nanotubes in a strong axial dc field at room temperature is presented. Negative differential conductivity is predicted. It is shown that $|dI/dV|$ for metal carbon nanotubes in the region of the negative differential conductivity significantly exceeds corresponding values for semiconducting ones. The predicted effect would enable the design of wave-generating nanotube-based diodes for submillimeter and infrared ranges.

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Since the discovery by Iijima [1] of carbon nanotubes (CNs), a great deal of interest has been focused on these quasi-one-dimensional monomolecular structures because of their unique physical properties (mechanical, electrical, optical, etc.) and the rapid experimental progress in the controlled preparation. Processes of electron transport in strong external fields when nonlinear effects are constitutive are of great interest for potential applications in nanoelectronics and for the experimental diagnostic of CN themselves.

The current-voltage (I-V) characteristics for tunneling electrons in individual single-wall CNs at low temperatures were measured in Refs. [2,3]. At such temperatures $k_B T \ll \mathcal{E}_c, \Delta\mathcal{E}$ and conduction occurs through well separated discrete electron states; here k_B is the Boltzmann constant, T is the temperature, $\mathcal{E}_c$ is charging energy, and $\Delta\mathcal{E} = \pi\hbar v_F/L$ is the energy level spacing, with v_F as the Fermi speed and L as the CN length [4]. At the above condition, the current is produced by the electrons tunneling through CN in the presence of the Coulomb blockade induced by the long-ranged (unscreened) Coulomb interaction. Consequently, the I-V characteristics observed in [2,3] are analogous to that obtained via the scanning tunneling microscopy [5]. As a result, at low temperatures the normalized differential conductivity $(V/I)\,(dI/dV)$ proves to be proportional to the local density of states. Therefore, the I-V characteristics reported in Refs. [2,3,5] provide significant information concerning the electron structure in CNs. On the other hand, the tunneling in macromolecules (in particular, CNs) can serve as a basis for the design of monomolecular transistors [6,7].

In this Letter we report a theoretical phenomenological analysis of the I-V characteristics of CNs at room temperatures, when $k_B T > \mathcal{E}_c, \Delta\mathcal{E}$. In our case, the current is produced by free charge carriers—quasiparticles which are π electrons moving in the field of the crystalline lattice. The nonlinearity of the I-V characteristic appears due to the nonlinear properties of the quasiparticle gas. We predict the *negative differential conductivity* (NDC) $dI/dV < 0$ in CNs in a certain range of the field strength.

Let us consider an undoped single-wall zigzag CN $(m, 0)$ exposed to a homogeneous axial dc field E_z, $E_z = V/L$, where V is the voltage between the CN ends. We shall apply the semiclassical approximation considering the motion of π electrons as a classical motion of free quasiparticles with dispersion law extracted from the quantum theory. With the account to the hexagonal crystalline structure of CNs, the tight-binding approximation gives [8]

$$\mathcal{E}(s\Delta p_\phi, p_z) \equiv \mathcal{E}_s(p_z) = \pm\gamma_0\left[1 + 4\cos(ap_z)\cos\left(\frac{a}{\sqrt{3}}\,s\Delta p_\phi\right) + 4\cos^2\left(\frac{a}{\sqrt{3}}\,s\Delta p_\phi\right)\right]^{1/2}. \quad (1)$$

Here $\gamma_0 \sim 3.0$ eV is the overlapping integral, $a = 3b/2\hbar$, and $b = 1.42\ A$ is the C-C bond length. The $-$ and $+$ signs correspond to the valence and conduction bands, respectively. In view of the transverse quantization of the quasimomentum, its transverse component can take m discrete values, $p_\phi = s\Delta p_\phi = \pi\sqrt{3}\,s/am$ $(s = 1, \ldots, m)$. Different from p_ϕ, we assume p_z continuously varying within the range $0 \le p_z \le 2\pi/a$, which corresponds to the model of infinitely long CN ($L = \infty$). This model is applicable to the case under consideration because we are restricted to temperatures and/or voltages well above the level spacing [9].

The motion of quasiparticles in an external axial electric dc field is described by the Boltzmann kinetic equation:

$$eE_z\frac{\partial f(\mathbf{p})}{\partial p_z} = -\frac{1}{\tau}\left[f(\mathbf{p}) - F(\mathbf{p})\right], \quad (2)$$

where e is the electron charge, $F(\mathbf{p})$ is the equilibrium Fermi distribution function, and τ is the relaxation time. The relaxation term of Eq. (2) describes the electron-phonon scattering [10,11], electron-electron collisions, etc.

Utilizing the method originally developed in the theory of quantum semiconductor superlattices [12], we can construct an exact solution of kinetic Eq. (2) without assuming the electric field to be weak. First, note that the distribution function $f(\mathbf{p})$ is periodic in p_z with period $2\pi/a$. Then, taking into account the transverse quantization, the distribution function can be presented by

$$f(\mathbf{p}) = \Delta p_\phi \sum_{s=1}^{m} \delta(p_\phi - s\Delta p_\phi) \sum_{r\neq 0} f_{rs} e^{iarp_z}, \quad (3)$$

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where f_{rs} are coefficients to be found, and $\delta(x)$ is the Dirac delta function. The equilibrium distribution function $F(\mathbf{p})$ can be expanded in the analogous series with the coefficients as follows:

$$F_{rs} = \frac{a}{2\pi} \int_0^{2\pi/a} \frac{e^{-iarp_z}}{1 + \exp\{\mathcal{E}_s(p_z)/k_BT\}}\, dp_z\,. \quad (4)$$

Substitution of both expansions into Eq. (2) gives $f_{rs} = F_{rs}/(1 + i\tau r\Omega)$, where $\Omega = aeE_z$ is the Stark frequency.

The surface current density is defined by the integral over the first Brillouin zone:

$$j_z = \frac{2e}{(2\pi\hbar)^2} \iint_{1stBZ} f(\mathbf{p})\upsilon_z(\mathbf{p})\, d^2\mathbf{p}\,. \quad (5)$$

Further, taking into account the relation $\upsilon_z(p_z, s\Delta p_\phi) = \partial\mathcal{E}_s/\partial p_z$, we can represent $\mathcal{E}_s(p_z)/\gamma_0$ by Fourier series with the coefficients $\mathcal{E}_{rs}$ defined similar to (4): Then, in view of Eqs. (5) and (3), one can obtain

$$j_z(E_z) = -\frac{8e\gamma_0}{\sqrt{3}\,\hbar bm} \sum_{r=1}^{\infty} \frac{r^2\Omega\tau}{1 + (r\Omega\tau)^2} \sum_{s=1}^{m} F_{rs}\mathcal{E}_{rs}\,. \quad (6)$$

This equation states the basis for the evaluation of I-V characteristics. Let us estimate the restrictions to the theoretical approach being developed. As it has been stated above, the quasiparticles motion is described classically by Boltzmann Eq. (2). Thus, both interband transitions and quantum-mechanical corrections to the intraband motion are left out of account in this model. The first approximation is valid when the condition $\Omega \lesssim \overline{\omega}$ holds true, whereas the condition $\Omega \lesssim \delta\mathcal{E}/\hbar$ must be fulfilled to utilize the second one. In the above inequalities, $\overline{\omega}$ is the low-frequency edge of the optical transition band, and $\delta\mathcal{E}$ is the width of the allowed band. For metal CNs, the order-of-magnitude estimate of the edge frequency is stated as $\overline{\omega} \sim 3\gamma_0 b/2\hbar R$ [13], where R is the CN's radius. Taking into account that $\delta\mathcal{E} \sim \gamma_0$, both restrictions on the Stark frequency impose the limitation on the external electric field strength: $|E_z| \lesssim \gamma_0/2eR$.

The Coulomb electron-electron interaction has been also left out of account in our approach. The role of this mechanism as applied to CNs was considered in a number of papers [9,14–16]. It has been established that the short-range electron-electron interaction, typical for CN arrays ("ropes"), have only weak effects at high temperatures. Since the Coulomb interaction in an isolated CN is unscreened, it manifests itself in another way providing an observable effect in a wide range of temperatures. Therefore, the results obtained on the basis of our model are mainly applicable to CN ropes. For an individual CN, this model must be modified taking into account the long-range Coulomb interaction. As it follows from Ref. [9], the change of the parameter τ temperature dependence is expected as the only result of the Coulomb interaction.

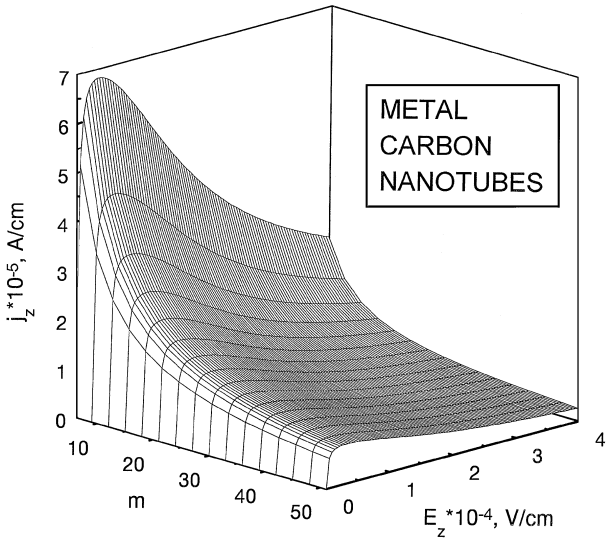

FIG. 1. I-V curves for metal zigzag carbon nanotubes, $T = 287$, 5 K, $\tau = 3 \times 10^{-12}$.

The I-V characteristics obtained via numerical calculation of Eq. (6) are presented in Fig. 1 for metal ($m = 3q$, q is an integer) and Fig. 2 for semiconducting ($m \neq 3q$) zigzag CNs. The figures show the linear dependence of j_z on E_z at weak strengths of the external field; it corresponds to the region of Ohmic conductivity. As E_z increases, the value $\partial j_z/\partial E_z$ grows smaller, and at $E_z = E_z^{(\max)}$ the current density reaches the maximum value $j_z^{\max}$. Further increase of E_z results in the decrease of j_z. Thus, we predict the region with the negative differential conductivity $\partial j_z/\partial E_z < 0$, in the I-V characteristics of CNs.

The external field strength $E_z^{(\max)} \approx 3.2 \times 10^3$ V/cm for the NDC region appears to be unexpectedly weak because the nonlinearity in the structure under consideration is determined by the value of aE_z; quantum superlattices

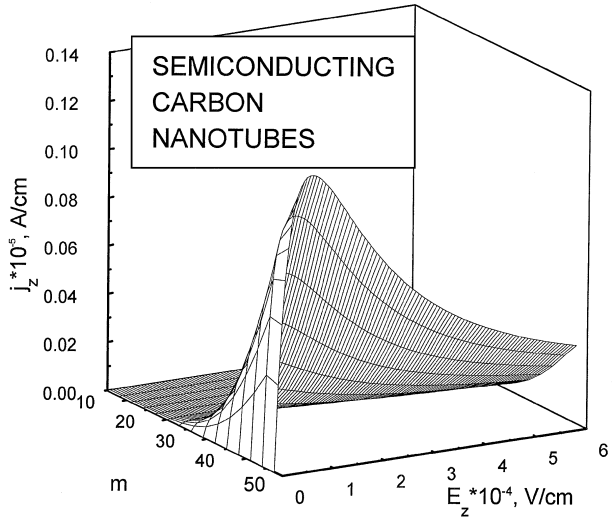

FIG. 2. I-V curves for semiconducting zigzag carbon nanotubes, $T = 287$, 5 K, $\tau = 3 \times 10^{-12}$.

with periods about 10^{-6} cm [12,17], much larger than b, show approximately the same fields for the NDC manifestation. It means that the nonlinearity in CNs is much higher than in superlattices. To explain this fact, let us compare the mechanisms of the nonlinear conductivity in CNs and in the superlattices. The quantum superlattices are formed by alternating plain layers of different semiconducting materials [12], while the lateral superlattices consist of 1D chains of identical and identically coupled GaAs/AlGaAs quantum dots [17]. Both structures are characterized by the dispersion law $\mathcal{E}(\mathbf{p}) = \Delta[1 - \cos(\tilde{a}p_z)]$, with Δ as the overlapping integral and $\tilde{a} = 2a/3$. Applying the method described above to this dispersion law, one can obtain the relation

$$j_z(E_z) = \sigma_{zz}E_z/(1 + \Omega^2\tau^2), \qquad (7)$$

instead of Eq. (6). Here $\sigma_{zz} = \lim_{E_z\to 0}(\partial j_z/\partial E_z)$ is the linear conductivity. Comparing two equations for the current density, we can conclude that the specific peculiarity of the CNs is the presence of the *high Stark components* [summation with respect to r in Eq. (6)] which are absent in (7).

It has been shown in Ref. [12] that the electron motion in the dc field can be described as the oscillations of an ensemble of effective harmonic oscillators (Stark components) [18] with the frequencies $r\Omega$. The full current is a superposition of partial currents of the Stark components. Their electrical field strength corresponding to the maximum current of the rth Stark component decreases with r as r^{-1} while our calculations show that oscillator strength of these component decreases slowly. This is due to the hexagonal crystalline structure of CNs reflected in dispersion law (1). The number of the unneglectable components is 70–150 for metal and 200–300 for semiconducting CNs. As a result, the role of the high Stark components in CNs is essential and the integral nonlinearity of the CNs is much higher than in superlattices [12,17]. The dependencies of j_z on Ω for CNs and 1D superlattice are compared in Fig. 3. The difference between the main Stark frequencies in the NDC region in metal zigzag CN (curve 3) and 1D superlattice (curve 1) is about 2 orders.

Let us estimate the possibility to observe the effect under discussion in doped CNs (BC_2N tubes). Such tubes have rectangular crystalline lattice and, according to [19], their dispersion law is similar to that of the 1D lattices. Therefore, the NDC effect in BC_2N tubes is expected to appear at larger field strength comparing with undoped CNs.

Figures 1 and 2 demonstrate that $E_z^{(\max)}$ depends on neither number m nor the conductivity type (metal or semiconductor), whereas, $j_z^{\max}$ shows the different dependencies on m for metal and semiconducting CNs. For metal CNs, $j_z^{\max}$ decreases with m while it increases for semiconducting ones. As $m \to \infty$, $j_z^{\max}$ for metal and semiconducting CNs tends to the same limit from opposite sides. Generally, at large m, the I-V characteristics of different

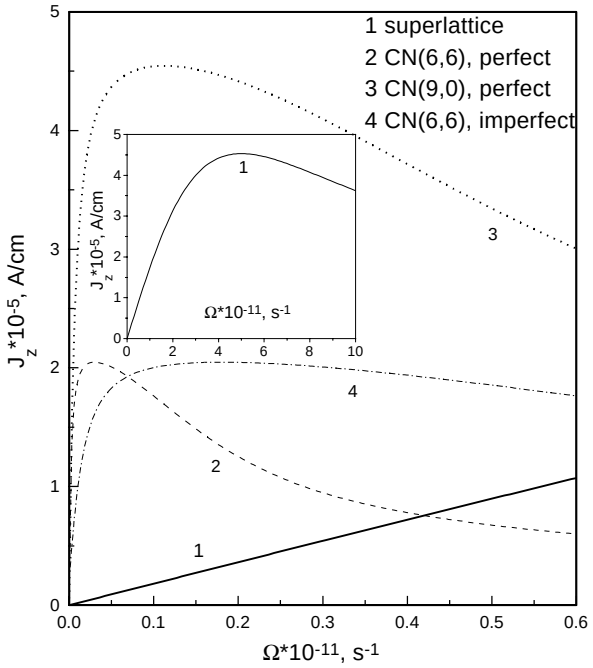

FIG. 3. Comparison of I-V curves for metal carbon nanotubes and superlattice, $T = 287,\ 5$ K, $\Delta = 3$ eV, $\tau = 3 \times 10^{-12}$, $\tau_{\text{eff}} = 5 \times 10^{-13}$.

CNs are coming close and in the limit case $m \to \infty$ they reduce to I-V characteristic of the plane graphite monolayer. It should be noted that the metal CNs exhibit much larger NDC as compared to semiconducting ones.

The reported theory was also applied to armchair CNs characterized by the dual index (m, m). The mathematical formalism of the theory is the same as described above; the only difference appears in the dispersion law [8]. The calculations give the I-V curves qualitatively similar to those represented in Fig. 1. However, at small m the magnitudes of $E_z^{(\max)}$ and $j_z^{\max}$ turn out to be less than for zigzag CNs with similar radius by the factor approximately 2. Different from zigzag CNs, the increase of m leads to the $E_z^{(\max)}$ growing up, and I-V curves for zigzag and armchair CNs become practically identical at $R > 20$ nm. Curve 2 in Fig. 3 represents the I-V characteristic of (6,6) armchair CN [20].

In our calculations, we assumed the relaxation time τ to be constant for all CNs. Actually, for the electron-phonon scattering and, in particular, for the electron scattering by twistons (thermally activated twist deformations of the tube lattice), τ is proportional to m [11]. To investigate this effect, we have calculated the I-V curves of armchair CNs with $\tau = m(8\pi^2 c_t/9\beta^2 k_B T v_F)$ [11], where c_t is the specific twist modulus, and β gives the linear dependence of the bond hopping operator on bond length. The calculations have shown that the scattering by twistons increases $E_z^{(\max)}$ and decreases $|\partial j_z/\partial E_z|$ in the NDC region; the less m, the stronger this effect. Quantitative changes of the I-V curves turn out to be insignificant in comparison with the case of $\tau = \text{const}$.

The presence of impurities and lattice defects provides one more channel of scattering of charge carriers. This mechanism can be described qualitatively by the substitution $\tau \rightarrow \tau_{\text{eff}} = \tau\tau_1(\tau + \tau_1)^{-1}$, where τ_1 is the relaxation time due to the impurity. The I-V characteristic of the imperfect (6,6) CN is shown in Fig. 3 (curve 4). By virtue of $\tau_{\text{eff}} < \tau$, the impurity effect results in the $E_z^{(\max)}$ increase and, in the NDC region, $|\partial j_z/\partial E_z|$ decrease.

In summary, we have predicted the NDC effect in CNs, which is expected to be observable in sufficiently long CNs at room temperatures. Note that the NDC provides the current instability. It can be expected that simultaneously applied dc and ac fields will result in the dynamic electron localization (which is the nonlinear phase of the instability) and in the 2D analog of the self-induced transparency, like it takes a place in the semiconducting superlattices. The above-mentioned effects are responsible for the absolute negative conductivity which thus is predicted to be exhibited in CNs. It must result in the appearance of the absolute negative conductivity zones and active properties of CNs providing a potentiality for the design of generative nanodiodes in microwave and infrared ranges. Such a possibility relates to both single CNs and CN ropes.

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