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Published in: Physical Review B - Condensed Matter and Materials Physics

DOI: 10.1103/PhysRevB.91.035428

Publication date: 2015

Link to publication
Citation for published version (HARVARD):

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Transport regimes in nitrogen-doped carbon nanotubes: Perfect order, semi-random, and random disorder cases

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The electronic structure and the transport properties of nitrogen-doped carbon nanotubes are investigated using a tight-binding model and a real-space Kubo-Greenwood approach, respectively. The transport regimes of various axial and helical doping configurations, from perfectly periodic to fully random disordered cases, are examined through the time dependence of the diffusivity. By varying the degree of disorder, a rich set of transient regimes is predicted going from persisting quasiballistic to momentarily localized regimes. A spectacular long-time ballistic regime is also observed for a specific semi-random disorder doping configuration owing to symmetry effects.

DOI: 10.1103/PhysRevB.91.035428 PACS number(s): 73.63.Fg, 72.10.—d, 72.15.Rn, 73.23.—b

I. INTRODUCTION

Electronic transport in one dimensional (1D) systems is very sensitive to the presence and type of disorder. In particular, intrinsic defect impurities such as doping with substitutional foreign atoms induce usually strong resonant backscattering. Actually, whatever the strength of the disorder, all the electronic states are localized in disordered 1D systems in the thermodynamical limit according to the scaling theory of localization [1–5]. However, a broad variety of disorder exists, from perfectly periodic to fully random disordered cases, examined through the time dependence of the diffusivity. By varying the degree of disorder, a rich set of transient regimes is predicted going from persisting quasiballistic to momentarily localized regimes. A spectacular long-time ballistic regime is also observed for a specific semi-random disorder doping configuration owing to symmetry effects.

II. COMPUTATIONAL METHODS

A. Effective tight-binding Hamiltonian

The CNT wave functions are expanded in a basis set of localized and orthogonal atomic orbitals. In this tight-binding framework, the Hamiltonian matrix elements are parametrized such that the electronic band structure reproduces the \( \text{ab initio} \) results. In the present study, a single \( \pi \) orbital per atomic site is used with first nearest-neighbors interaction hopping parameter set to \(-2.72\) eV. The N impurity potential is considered as a perturbation of on-site terms on the N atom and on the C atoms up to the critical distance \(d_c = 7.5\) Å [20–22]. The on-site parameter is taken as zero otherwise to align the Fermi energy of the perfect CNT to zero. The minimal distance between two consecutive N atoms \((d_{\text{NN}})\) is always kept greater than twice \(d_c\) such that the overlap of individual N impurity potentials is avoided. (See Refs. [16,23,24] for details regarding the TB parametrization.)

B. Kubo-Greenwood transport approach: Ballistic, diffusive, and localized regimes

The real-space Kubo-Greenwood transport approach [17–20,25,26], used throughout the present study, focuses on the evaluation of the electronic diffusivity \((D)\) from which the transport regimes can be identified as ballistic, diffusive, or
localized. The diffusivity is computed for each energy \( E \) as function of the time \( t \). \( D(E,t) \) gives an insight on the diffusion process occurring at different time scale. At short time, or equivalently at short propagation distances, the transport is ballistic and \( D(t) \) increases linearly with time, the slope being the square of the average carrier velocity \( (v^2) \). At an intermediate time scale (intermediate propagation distances), the diffusivity usually undergoes a sublinear regime because of the first scattering processes with defect impurities. Later, i.e., when enough random scattering processes occurred, the propagation reaches a (thermodynamical) steady state, also called the diffusive regime. In this regime the diffusivity saturates to a maximal value \( [D(t) \to D_{\text{max}}] \). At (infinitely) long time, the diffusivity either stays in the diffusive regime or decreases to zero \( [D(t) \to 0] \) if localization phenomena occur. According to the scaling theory of localization \([2,5] \), all states are localized in the disordered 1D system; hence diffusivity should always drop to zero at long time. If the system is periodic, i.e., ordered, the diffusivity behavior at infinitely long time is the ballistic regime, which means \( D(t) \to \infty \) with a linear increase.

III. PERFECT CNT, PERIODICALLY, AND RANDOMLY N-DOPED CNTS

We consider here perfect, periodically, and randomly N-doped (10,10) CNTs as a model system for metallic CNTs. The unit cell of an armchair (10,10) CNT is composed of 40 atoms which can be sliced along the tube axis into two carbon layers with a tenfold rotational symmetry [top panel in Fig. 1(a)]. In order to ensure a constant concentration of nitrogen, we consider supercells of \( n_{\text{cell}} (10,10) \) unit cells with one N atom per supercell. Following the long-range symmetry effects found in Ref. [16] we restrict ourselves to \( n_{\text{cell}} \) equal to a multiple of 3. Consequently, we choose \( n_{\text{cell}} = 24 \) inducing a concentration of chemical dopants of \( \sim 0.1\% \). Since the perfect and the periodically N-doped CNTs are both periodic structures, the Bloch theorem can be applied and hence the band structures of these two systems can be examined [Fig. 1(b) and Fig. 1(c), respectively]. In the random N-doping case, only the density of states (DOS) is accessible. It is computed using the Haydock recursion method \([27]\) applied to a sufficiently long disordered CNT (the system length is \( L_{\text{sys}} = 160d_{\text{sc}} = 945 \) nm). The DOS of the three systems are depicted in Fig. 1(d). In Fig. 1(b), the band structure of the perfect (10,10) CNT is simply folded back into the reduced Brillouin zone (BZ) by the artificial supercell translational symmetry. In Fig. 1(c), this band structure is perturbed by the substitution of one N for a C atom. The periodic arrangement of the N dopants introduces a defect band (in the energy window \([0.56,0.59] \) eV) because of the breaking of the original unit cell translational symmetry of the perfect structure (although a translational symmetry exists at the scale of the supercell). Consequently, pseudogaps appear at \( \Gamma (k = 0) \) and \( \chi (k = \pi/d_{\text{sc}}) \), providing splitting effect on the band structure of the perfect system and the loss of transmission channels near the Fermi energy \( E_F \) and around the defect energy \( (E_d) \) associated to the defect band \([16,24]\). These pseudogaps correspond to the plateau dips appearing in the DOS indicated by arrows in Fig. 1(d) (black curve). Moreover, when a random distribution of the N atoms is considered, the pseudogaps completely disappear in the corresponding DOS. However, allowed minibands seem to be still present around \( E_d \) (small bump in the DOS), and splitting on the van Hove singularities is maintained at higher energies, i.e., around \( E \sim \pm 0.9 \) eV.

The square modulus of the electronic wave functions of the perfect and the periodically N-doped systems at the \( \Gamma \)
function of the perfect CNT (which conserves the symmetry pattern of the original wave function), which deviates from the perfect CNT, a less localized state is observed from the original ones. However, for the bands that deviate to pseudogap band edge states, i.e., bands that largely deviate for the perfect CNT (similar annular pattern with the same period described above), strongly or slightly localized states around the defect energy \( E_d \) but still extended states elsewhere. A ruler is given as a guide for the eyes to ease comparison between periodic patterns observed in the perfect CNT and the reminiscent periodic patterns observed for the slightly localized states in the N-doped CNT.

The real-space Kubo-Greenwood approach is now used to examine diffusion processes in the three systems, i.e., perfect, periodically N-doped, and randomly N-doped CNTs. In particular, the nature of the propagating modes around the defect energy \( E_d \) is scrutinized by following the time dependence of the diffusivity \( D(t) \). As already mentioned, in the periodically N-doped case, the appearance of a defect band (orange line in top panel of Fig. 3) creates localized states which give rise to an enhanced DOS as illustrated in Fig. 3 by the two peaks at the energies \( E_{d1} \) and \( E_{d2} \). The exact energy position of these two peaks depends on the accuracy level of the technique used to compute the DOS. In Fig. 3, the DOS computed from the band structure using a small broadening parameter \( (\eta = 1 \text{ meV}) \) (dashed lines), and the DOS computed from the recursion technique (RT) (thick lines) are compared. For a very accurate DOS calculation from the electronic band structure \( (\eta = 1 \text{ meV}) \), the DOS peaks are found to be well aligned with the upper and lower bounds of the defect band \( (i.e., E_{d1} = 0.562 \text{ eV and } E_{d2} = 0.588 \text{ eV}) \). However, the use of the RT yields a lower level of accuracy and the defect energies are positioned at \( E_{d1} = 0.565 \text{ eV and } E_{d2} = 0.583 \text{ eV} \) (indicated by arrows).

These two propagating modes in the perfect CNT, almost indistinguishable in Fig. 4(a) (full and dashed blue curves), exhibit a linear dependency \( [D(t) = v_0 t] \), endorsing the ballistic transport regime \( (v_0 \text{ is the ballistic velocity}) \). However, when a randomly N-doped CNT is considered, the propagating modes around \( E_d \) become localized and the corresponding \( D(t) \) starts decreasing exponentially \( [D(t) = D_{\text{max}} e^{-\alpha t}\text{ for }\alpha \text{ short time } (t_0 = 25 \text{ fs})] \) by a short time \( (t_0 = 25 \text{ fs}) \) [Fig. 4(a), red curves]. The localization effects for random distribution have been described by Latil et al. [20] and discussed a few years later as an experimental evidence of the Anderson localization phenomena at the mesoscopic scale [29–31]. In opposition with the perfect

![Figure 2](image)

**FIG. 2.** (Color online) Square modulus of the eigenfunctions of the perfect and periodically N-doped CNTs, at the \( \Gamma \) point and for different energies. All the eigenfunctions of the perfect CNT are extended states, while eigenfunctions of the periodically N-doped CNT are either strongly or slightly localized states around the defect energy \( (E_d) \) but still extended states elsewhere. A ruler is given as a guide for the eyes to ease comparison between periodic patterns observed in the perfect CNT and the reminiscent periodic patterns observed for the slightly localized states in the N-doped CNT.
and the randomly N-doped structures, the periodic doping scheme presents an interesting sequence of diffusion regimes [Fig. 4(a), black curves], especially at $E = E^2_d = 0.583$ eV. At short propagation times, $D(t)$ follows the same behavior as for random disorder, i.e., a very short ballistic regime followed immediately by the onset of a localization regime and hence an exponential decrease of $D(t)$. However, this is a transient regime since after a short while ($t > 150$ fs), the diffusion process of the propagating wave packet changes drastically and at longer times, $D(t)$ behaves linearly $D(t) = v^2_1 t$ meaning that ballisticlike propagating modes are observed. The short- and long-time ballistic velocities, $v_0(E)$ and $v_1(E)$, respectively, are depicted in Fig. 4(b) as a function of the energy for the periodically N-doped structure. At short times, the propagating modes are only slightly perturbed by the defect. In fact, the short-time velocities $v_0$ of both the periodically N-doped CNT (continuous dark curve) and the perfect CNT are similar (continuous blue curve), and agree well with the average group velocity determined from the band structure, $v_{\text{BS}}$, of the perfect CNT (blue dashed curve with circle symbols). However, at long times, the propagating modes become more sensitive to the presence of the periodic defect. The ballisticlike velocity $v_1$ decreases significantly (dark dotted-dashed curve) and the ratio $v_1/v_0$ gets minimal at the defect energies $E^1_d$ and $E^2_d$, i.e., 0.15 and 0.07, respectively. The diffusivity $D(t)$ gives here more information than the band structure, in the sense that before reaching the long-time ballistic regime, intermediate transport regimes can be captured and two distinct velocities can be calculated. From a propagation point of view, the electrons first experience the perfect CNT on a very short length scale ($\lesssim d_{N-N}$). Then, electrons are progressively scattered by the N atoms but, after a while ($\sim 3-4 d_{N-N}$), the periodic arrangement of the N atoms reveals to electrons the ordered nature of the system. Interferences occur and the electrons end up into the supercell Bloch states. At this stage, the ballistic regime is recovered with velocities $v_1$ corresponding to the group velocities as determined from the supercell band structure $[v_{\text{BS}}$, dark dashed curve with circle symbols]. One also notes that in the shaded region, which corresponds to the small band gap visible in Fig. 3(b), the values of $v_1$ are numerically ill-defined because of a nonexactly zero value of the DOS.

IV. AXIAL SEMI-RANDOM CONFIGURATION

In comparison with the previous periodic doping scheme, a constrained randomness of the dopant positions in the
diffusive regime is observed at long times, without any signs of localization effects (which may appear at even longer time scale). A localized transport regime is however obtained for the propagation mode at $E_D^1$ but only beyond $t_0 = 500$ fs. This value of $t_0$, establishing the onset of localization, is considerably larger than for totally random configuration [$t_0 = 25$ fs, Fig. 4(a)]. It is important to emphasize that for a rather long intermediate time scale ($\sim 2$ ps), $D(t)$ is quantitatively higher in this axial semi-random doping scheme than in the periodic doping scheme. However, this is only a transient behavior since in the thermodynamic limit, the electronic diffusion in periodic systems will always exceed the one in semi-random systems because of the linear increase of $D(t)$. Such a crossover is observed at $t \sim 2600$ fs for $E = E_D^1$ in Fig. 5(c). By comparing the fully random disorder case and the present axial semi-random doping scheme, it is obvious that although all states should be localized in disordered 1D systems according to scaling theory, the degree of localization and the rate of its effects on the diffusivity can greatly fluctuate.

V. HELICAL DOPING CONFIGURATIONS

A helical doping configuration is described by a screw operator $S(d, \theta)$. This operator is defined in the polar coordinates $(d$ and $\theta$) by an axial translation $d$ and a rotation with an angle $\theta$ that link two successive chemical defects (see Fig. 6) [32]. For the $(10,10)$ CNT, the position of 40 atoms in one unit cell admits a tenfold symmetry ($\theta_0 = 2\pi/10$) and can then be described by four atomic sites (A,B,C,D) [Fig. 6(a)]. The helical doping configurations considered in this section, $d$ is chosen as a multiple of $3d_0$ as before, and $\theta$ as a multiple of $\theta_0$. Therefore, the screw operator $S(d_n = 3nd_0, \theta_m = m\theta_0)$ can be simply noted as $S(n,m)$, $n$ and $m$ being integers. Within this screw operator notation, the doping schemes studied in previous sections are $S(8,0)$ (axial periodic doping), and $S(n,0)$ with random $n$ (axial semi-random doping).

The cases of the ordered and disordered helical doping configurations are now investigated. First, the ordered (periodic) helical configuration is considered with the screw operator $S(8,1)$ [Fig. 6(b)], i.e., $d_{N-N} = 24d_0$ and $\theta = \theta_0$. Then, angular disorder is introduced, keeping the axial ordering, i.e., $m$ equals a random integer [$(8,m)$, Fig. 6(c)]. Finally, both axial and angular parts are randomized but $d$ and $\theta$ are still multiples of $3d_0$ and $\theta_0$, respectively [$S(n,m)$, Fig. 6(d)]. The labeling of all the studied doping configurations using the screw operator notation are summarized in Table I.

The DOS of these three helical doping configurations together with the DOS of the periodic and axial semi-random doping configurations are depicted in Fig. 7(a). Then, $D(t)$ is illustrated in Fig. 7(b) for $E_D^1 = 0.565$ eV and $E_D^2 = 0.583$ eV. The DOS of the $S(8,0)$, $S(8,1)$, and $S(8,m)$ systems are qualitatively indistinguishable and $D(t)$ behave equivalently for these three doping configuration schemes even when $m$ takes random values. Indeed, the long-time ballisticlike permanent regime is spectacularly preserved even in the case of angular disorder although this structure does not possess any periodic arrangement. Furthermore, when the axial periodicity is broken, i.e., when both $n$ and $m$ take random integer values [$S(n,m)$], this particular rotational disorder does not destroy the features obtained for the previous case [$S(n,0)$].
The corresponding $D(t)$ shows both diffusive and localized transport regimes [Fig. 7(b)]. This result brings us to the conclusion that the diffusion process is not sensitive to the angular disorder as long as the armchair nanotube rotational symmetry ($\theta_0$) is conserved, i.e., all the N atoms occupy the equivalent position in the basis (A,B,C,D). These results justify the effect of rotational symmetry as recently presented in the electronic transport responses for armchair and chiral nanotubes at shorter length scale [16].

From the present analysis of the diffusion coefficients, it appears clearly that semi-random distributions of the N dopants can yield particularly good transport properties as compared to a random distribution. Indeed, the elastic mean free path of electrons reaches easily several $\mu$m for a semi-random configuration like $S(n,0)$ close to Dirac point region ($E = 0$ eV), while it hardly reaches 50 nm for a fully random distribution. Within the defect energy window [0.54–0.61] eV, the mean free paths are lowered and found in the range of [10–700] nm for the semi-random configuration, while it is constant and equal to 5 nm for the fully random case. Consequently, in N-doped CNT with semi-random distribution, the elastic scattering may not be anymore the limiting scattering mechanism and inelastic effects should become important depending on temperature and the applied bias voltage. At low bias, the experimental measurements reported inelastic mean free paths of the order of few $\mu$m [33] which correspond rather well with predicted values for electron scattering with acoustic phonons [33–35]. Elastic and inelastic scattering will therefore compete around $E = 0$ eV; however, close to the defect energy elastic scattering with N dopants should still be more efficient. At high bias, electrons have enough energy to emit optical and zone boundary phonons. The scattering with such phonons gives a much lower inelastic mean free path in the range [10–200] nm [33,36], and hence could become dominant in the present semi-randomly 0.1% N-doped CNTs.

### VI. CONCLUSION

The electronic transport regimes in N-doped carbon nanotube has been examined at the mesoscopic length scale using the Kubo-Greenwood formalism and an effective tight-binding approach. The propagating modes in the vicinity of the resonant defect energy have been identified from the time-dependent diffusion coefficient $D(t)$ for various doping configurations, including periodic, semi-random, and random distributions. In all periodic and semi-random doping schemes, the position of dopants is given from the screw operator $S(d_n, \theta_m) \equiv S(n,m)$ notation such as $d_n = 3n d_0$ and $\theta_m = m \theta_0$ are the axial and rotational translations, and where $3d_0$ is the Fermi wavelength while $\theta_0 = 2\pi/10$ corresponds to the tenfold rotational symmetry as defined in the (10,10) host CNT. Besides these periodic and semi-random systems, the perfect

<table>
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<th>Configuration label</th>
<th>Screw operator</th>
<th>Axial distribution</th>
<th>Angular distribution</th>
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<td>Perfect</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Axial periodic</td>
<td>$S(8,0)$</td>
<td>Ordered</td>
<td></td>
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<tr>
<td>Axial semi-random</td>
<td>$S(n,0)$</td>
<td>Semi-random</td>
<td></td>
</tr>
<tr>
<td>Helical periodic</td>
<td>$S(8,1)$</td>
<td>Ordered</td>
<td>Ordered</td>
</tr>
<tr>
<td>Helical angular semi-random</td>
<td>$S(8,m)$</td>
<td>Ordered</td>
<td>Semi-random</td>
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<tr>
<td>Helical semi-random</td>
<td>$S(n,m)$</td>
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<td>Random</td>
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TABLE I. (Color online) Labeling and screw operator notation of the different N-doped CNTs.

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CNT and the CNT with a completely random distribution of the N atoms have been considered as reference cases. For doping configurations with an axial periodicity [e.g., $n = 8$ in $S(n,m)$], ballistic-like transmission modes appear in the permanent regime [i.e., linear increase of $D(t)$] but with electronic velocities lower than in the perfect CNT and which correspond to the average group velocity determined from the band structure. It is interesting to note that as the tenfold rotational symmetry is kept along the structure [i.e., $m$ can take random integer values], the behavior of the diffusion coefficient $D(t)$ is invariant. Therefore, the semi-random $S(8,m)$ helical doping configuration exhibits also a ballistic regime.

For configurations with a semi-random axial distribution [i.e., $S(n,m)$ with $n$ a random integer], $D(t)$ changes drastically. In these semi-random axial cases, $D(t)$ is found to increase rapidly at the short and intermediate time scale (closer to the ballistic limit of the perfect CNT than the periodic axial configurations), but then saturates (diffusive regime) or even decreases (localization regime) at longer-time scale. Indeed, for the first defect energy ($E_{1d}$), the localization effects seem to be suppressed (or at least shifted to very long time), while quantum interferences leading to localization are well identified for the second defect energy ($E_{2d}$). The rapid increase of $D(t)$ at short-time scales suggests that for short enough CNTs and around the defect energy, such a semi-random axial disorder provides faster electronic diffusion and thus higher conductivities than with a periodic axial configuration. The study of such screw configurations of the disorder are important to understand the implications on the transport properties of the (quasi)periodic helical modifications such as obtained for CNTs wrapped with DNA (DNA-CNTs). These DNA-CNTs are used in particular for the sorting of CNTs in size and chiralities [14,15].

**ACKNOWLEDGMENTS**

H.K. and A.L. contributed equally to this work. H.K. was supported by the Fonds Spéciels de la Recherche (FSR) Incoming Post-doctoral Fellowship of the Académie universitaire Louvain, co-funded by the Marie Curie Actions of the European Commission (No. 4 9137 E1). A.L. and J-C.C. acknowledge financial support from the F.R.S.-FNRS of Belgium, from the Communauté Française de Belgique through the Action de Recherche Concertée (ARC) on Graphene Nanoelectromechanics (No. 11/16-037). Computational resources have been provided by the supercomputing facilities of the Consortium des Equipements de Calcul Intensif en Fédération Wallonie Bruxelles (CECI).

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