Conduction mechanism and magnetotransport in multiwall carbon nanotubes

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We report on a numerical study of quantum diffusion over μm lengths in defect-free multiwall nanotubes. The intershell coupling allows the electron spreading over several shells, and when their periodicities along the nanotube axis are incommensurate, which is likely in real systems, the electronic propagation is shown to be non ballistic. This results in magnetotransport properties which are exceptional for a disorder free system, and which help to understand the experiments.

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Carbon nanotubes are remarkable for their structure and electronic properties, and seem suitable for molecular electronic devices [1,4]. Single wall carbon nanotubes (SWNTs) can be either metallic or semiconducting depending on their helicity, i.e. how the graphene sheet is rolled up [2]. Experimentally, metallic SWNTs are very good conductors, exhibiting ballistic transport [3,4]. Structural disorder in these systems is very small leading to mean free path in the μm range [3].

Multiwall nanotubes (MWNTs) have a complex structure that consists of several shells sharing the same axis. Their electronic properties are complicated and less understood [3]. Indications for ballistic transport exist in some MWNTs [1], but the interpretation of quantized conductance n(2e²/h) with half integer values of n is controversial. Some authors propose an effect of contact between electrode and the nanotube [3] whereas others show that transport through several shells is essential [4]. Many evidences for diffusive regime and quantum interferences effects are also found in other experiments [1,9,11]. This has been interpreted as a result of scattering by structural or chemical disorder, but the mean free path has to be several orders of magnitude smaller than in SWNTs. Even in the limit of vanishingly small disorder, this raises fundamental questions such as: how many shells participate to transport, is it just the outer shell that carries current or are inner shells important? Is electronic transport ballistic in these systems?

In this Letter, we report the first theoretical study of quantum diffusion on the μ-meter scale for defect-free MWNTs. The effect of the interlayer coupling on the propagation of the wavepackets is analyzed. As the different shells periodicities along the nanotube axis are in general incommensurate, the system probed by the electron is not periodic, and we show that this yields intrinsic non ballistic transport. The consequences of this anomalous propagation on the magnetoconductance, are investigated for a magnetic field parallel to the nanotube axis. In particular, a negative magnetoresistance at low field is found, as well as oscillations of the conductance which are periodic with the magnetic flux Φ through each tube with a periodicity Φ_0/2 (Φ_0 the quantum flux). This offers an alternative explanation of the experimental results of Bachtold et al. [11] without assuming strong disorder.

Our model hamiltonian is a tight-binding one which is believed to provide a good description of the electronic structure of MWNTs. In this model, one p⊥-orbital per carbon atom is kept, with zero onsite energies, whereas constant nearest-neighbor hopping on each layer n (n.n.), and hopping between neighboring layers (n.l.) are defined by [12]:

\[ H = \gamma_0 \sum_{i,j \in n,n,n} |p'_i|^2 |p'_{j,n}| - \beta \sum_{i,j \in n,l} \cos(\theta_{ij}) e^{d_{ij} - d_{n,l}} |p'_i|^2 |p'_{j,l}| \]

where \( \theta_{ij} \) is the angle between the \( p'_i \) and \( p'_j \) orbitals, and \( d_{ij} \) denotes their relative distance. The parameters used here are: \( \gamma_0 = 2.9eV, a = 3.34A, \delta = 0.45A \) [12]. In this tight-binding approach, the differences between SWNTs and MWNTs stem from the parameter \( \beta \), as the limit \( \beta = 0 \) corresponds to uncoupled shells. Estimate gives \( \beta \approx \gamma_0/8 \) [12], but in order to get insight in the effect of \( \beta \) on transport properties, the cases \( 0 \leq \beta \leq \gamma_0 \) have been considered. Synthesized MWNTs contain typically a few tenth of inner layers but due to computer limitations, we have restricted our study to 2 and 3-wall nanotubes, taking the intershell distance of 3.4Å as in graphite.

By means of a powerful O(N) method based on development of the operator \( \exp(-iHt/h) \) in a basis of orthogonal polynomials [13], the time-dependent Schrödinger equation for the evolution of wavepackets (WP) \(|\psi\rangle\) up to large time, is solved. This allows us to calculate the spreading of the WP, defined as \( L_\psi(t) = \sqrt{\langle \psi | (X(t) - X(0))^2 |\psi\rangle} \) over micron length scales \((X(t)\) is the position operator along the tube axis in the Heisenberg representation). We also define the time-dependent diffusion coefficients, by \( D_\psi(t) = L_\psi(t)^2/t \). \( D_\psi(\tau_\phi) \) is the diffusivity along the nanotube axis, if at \( \tau_\phi \) the electronic wavefunction loses its phase memory due to some inelastic scattering. The diffusion coefficient at \( \tau_\phi \) is also connected to the Kubo conductivity \( \sigma = (e^2/h)\rho(D(\tau_\phi)) \), where \( \rho \) is the density of states, and \( \langle D(\tau_\phi) \rangle \) the average of diffusion coefficients for WP close to the Fermi level.
The wavepackets $|\psi\rangle$ are chosen localized on single sites of the nanotube at initial time, and by averaging over many sites, we obtain energy-averaged transport properties. The average spreading $L(t)$ and the average diffusion coefficient $D(t)$ are defined by $L(t) = \sqrt{\langle L_x^2(t) \rangle} = \sqrt{\langle D(t) \rangle}$, where $\langle \rangle$ denotes an average over many wavepackets. This provides a good qualitative picture of wavepacket propagation in MWNTs constituted of conducting shells. Note that experimental results suggest that Fermi energies away from the charge neutrality point are relevant [15,16]. Recently, Krüger et al. obtained variations of the Fermi energy of ±1 eV, corresponding to 10 – 15 conducting channels instead of 2 per metallic layer [16].

An essential geometrical remark is that depending on their helicities $(n, m)$, two shells of a given MWNT are commensurate (resp. incommensurate), if the ratio between their respective unit cell lengths $T_{(n,m)}$ along the tube axis is a rational (resp. irrational) number [3]. From geometrical considerations, one expects that incommensurate structures are more likely than commensurate structures. As shown in this work, this issue has deep consequences on the conduction mechanism intrinsic to MWNTs.

As representative cases of commensurate systems, we have considered $(9,0)@(18,0)$ and $(6,6)@(11,11)@(16,16)$ $(T_{(9,0)} = T_{(18,0)} = 3a_{cc}$ and $T_{(6,6)} = T_{(11,11)} = T_{(16,16)} = \sqrt{3}a_{cc}$, where $a_{cc} = 1.42\text{Å}$ is the interatomic distance between carbon atoms). As representative cases of incommensurate systems, we have considered $(9,0)@(10,10)$ and $(6,4)@(10,10)@(17,13)$ $(T_{(6,4)} = 3\sqrt{19}a_{cc}$, $T_{(10,10)} = \sqrt{3}a_{cc}$, and $T_{(17,13)} = 3\sqrt{679}a_{cc}$).


**Interlayer electronic transfer.** The spreading of a WP, initially localized at one site of the outer shell, is followed on the different shells (Fig.1). Only two representative cases of 3-wall systems are reported. In commensurate systems, a rapid change in the weight of the wavefunction on each shell is followed by a relaxation at the time scale of $\tau_0 \sim h\gamma_0/\beta^2$, in good agreement with the Fermi Golden Rule. By changing the amplitude of $\beta$ in the range $[\gamma_0/8, \gamma_0]$, the expected scaling form of $\tau_0$ is checked. Note that for two electrodes separated by 1µm and assuming ballistic transport with a Fermi velocity of $10^6\text{ms}^{-1}$, the corresponding time is $t \sim 4500\text{h}/\gamma_0$. This is two orders of magnitude larger than $\tau_0$ (for $\beta = \gamma_0/8$), and points towards an important contribution of interwall coupling in experiments. In the incommensurate systems, a continuous decay from the outer shells to the inner shells is also found with similar characteristics.

![FIG. 1. Temporal repartition of the wavepacket over the 3 shells. The initial state is localized on the outer shell ((16, 16) or (17, 13)). Time is in $\hbar/\gamma_0$ units and $\beta = \gamma_0/3$.](image1)

**Quantum diffusion along the nanotube axis.** A fundamental difference between commensurate and incommensurate systems is manifested in the quantum diffusion properties (Fig.2). In commensurate systems, $L(t)$ is found to follow a ballistic law: $L(t) = vt \rightarrow D(t) = v^2t$. This is expected on the basis of band structure theory for periodic systems. The velocity $v \simeq 5.10^3\text{m.s}^{-1}$, deduced numerically, is close to the averaged Fermi velocity of one isolated shell. It is nearly independent on $\beta$ and depends weakly of the shells constituting the MWNT.

In the 2-wall incommensurate system, we observe an anomalous diffusion $L(t) \sim t^\eta$, $\eta = 0.88$ (Fig. 2), for $\beta = \gamma_0/3$, intermediate between ballistic ($\eta = 1$) and diffusive ($\eta = 1/2$) motions. Anomalous diffusion laws are also observed in quasiperiodic systems, which present a particular repetitivity of local environments [3,7].

In the 3-wall incommensurate systems, a saturation of the diffusion coefficient is seen at large time, which is equivalent to a diffusive-like behavior ($L(t) \sim \sqrt{t}$) as observed in disordered systems. This allows to define an effective mean free path $\tilde{l}_c$ and an effective scattering time $\tilde{\tau}_s$ from $\lim_{t \rightarrow \infty} D(t) = D_0 = \tilde{l}_c \tilde{\tau}_s \equiv v^2\tilde{\tau}_s$, where $v^2$ is

![FIG. 2. Main frame: Diffusion coefficients for typical 2-wall and 3-wall commensurate and incommensurate MWNTs (for $\beta = \gamma_0/3$) as a function of propagation time (in $\hbar/\gamma_0$ units). Inset: Same quantity for the (6, 4)@(10, 10)@(17, 13) with $\beta = \gamma_0/8$.](image2)
the slope of $D(t)$ at origin. One can estimates an effective elastic mean free path $\tilde{l}_e \simeq 35 \text{ nm}$ for $\beta = \gamma_0/3$ (Fig.3). Note that a diffusive law is also observed in the Harper model with a weak incommensurate potential \[18\].

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parameters incommensurate cases, with the same hamiltonian pa-

systems, in which the quantum diffusion is weakly depen-

number of shells. Contrary to the case of commensurate

3-wall incommensurate system varies between 35

β

3-wall, the diffusion regime for

γ

2-periodic oscillations of the con-

0.25 0.5 0.75 1

3

0

a Peierls substitution : hopping terms have a field-
dependent phase $e^{i\phi}$ with $\phi_{ij} = \frac{\Phi}{\ell} \int_{ij} A \cdot dr$, where $A$ is the vector potential. We look at $D(\tau_\phi, \Phi)$, where $\Phi$ is the flux of the magnetic field through the tubes and is identical for all tubes. It is sufficient to consider $0 < \Phi < \Phi_0$ since at least a $\Phi_0$-periodicity is expected from gauge invariance \[18\]. We assume that variations of the diffusivity give the main contribution to magneto-

cutance.

FIG. 3. Main frame : $D(\tau_\phi, \Phi)$ (in $\text{Å}^2 \gamma_0/h$ unit) for a metallic SWNT (9,0) evaluated at time $\tau_\phi \gg \tau_e$, for two disorder strengths, $V_4/\gamma_0 = 3$ and 1, such that the mean free path ($l_e \sim 0.5$ and 3 nm, respectively) is either shorter (dashed line) or larger (solid line) than the nanotube circumference ($C \sim 2.3 \text{nm}$). The right y-axis is associated to the dashed line and the left y-axis to the solid line. Inset : $D(\tau_\phi, \Phi)$ for $l_e = 3 \text{ nm} > C$ and $L(\tau_\phi) < 2l_e$.

The striking difference between the 2-wall and 3-wall incommensurate cases, with the same hamiltonian parameters $\beta$ and $\gamma_0$, shows that the diffusion regime for incommensurate MWNTs is very sensitive to the geometrical relation between the different shells and to the number of shells. Contrary to the case of commensurate systems, in which the quantum diffusion is weakly dependent on $\beta$, the diffusion law is sensitive to the value of $\beta$. For example, for $\beta$ varying between $\gamma_0/3$ and $\gamma_0$, the diffusion exponent for the 2-wall varies between $\eta = 0.88$ and $\eta = 0.75$, and the estimated mean free path for the 3-wall incommensurate system varies between 35nm and 2nm. For $\beta = \gamma_0/8$, the diffusive regime in the 3-wall is not reached in the evolution time accessible to the com-

putation (inset of Fig 2).

Transport in a magnetic field.-Applying a magnetic field parallel to the MWNT axis, Bachtold et al. \[11\] have reported negative magnetoresistance at low field (decrease of the resistance with increasing magnetic field strength) as well as $\Phi_0/2$ periodic oscillations of the conductance, well described by the weak localization (WL) theory \[20\]. They correlate this effect to an intrinsic dis-

order and assume that the current is carried only by the outer nanotube shell.

In order to get insight in the origin of these experi-

mental results, we compare two situations. In the first situation (case-I), similar to the one considered by Bachtold et al. \[11\], the coupling between the outer and inner shells is neglected. This corresponds to $\beta = 0$, which is equivalent to a SWNT. A substitutional disorder is intro-

duced by a random modulation of onsite energies in the range $[-V_4/2, V_4/2]$, in order to tune the value of the mean free path, since $l_e \propto 1/V_4^2$ in the limit of weak scatter-

ing. In the second situation (case-II), we consider a MWNT with $\beta \neq 0$ but we neglect disorder.

The magnetic field modifies the hamiltonian through a Peierls substitution : hopping terms have a field-
dependent phase $e^{i\phi}$ with $\phi_{ij} = \frac{\Phi}{\ell} \int_{ij} A \cdot dr$, where $A$ is the vector potential. We look at $D(\tau_\phi, \Phi)$, where $\Phi$ is the flux of the magnetic field through the tubes and is identical for all tubes. It is sufficient to consider $0 < \Phi < \Phi_0$ since at least a $\Phi_0$-periodicity is expected from gauge invariance \[18\]. We assume that variations of the diffusivity give the main contribution to magneto-

cutance.

Case-I (see Fig.3). Several types of situations occur depending on the relative values of $L(\tau_\phi)$, $l_e$, and $C$, which are respectively the average spatial extension of WP at the time $\tau_\phi$, the elastic mean free path, and the circumference of the nanotube. When $l_e < C < L(\tau_\phi)$, our calculations confirm that the behavior of $D(\tau_\phi, \Phi)$ follows WL theory predictions. The diffusivity increases at low field (negative magnetoresistance) and presents a $\Phi_0/2$-periodic Aharonov-Bohm oscillation, i.e. $D(\tau_\phi, \Phi + \Phi_0/2) = D(\tau_\phi, \Phi)$ (see Fig.3). For a smaller disorder with $l_e > C$, depending on the value of $\tau_\phi$, two different behaviors are obtained. If $L(\tau_\phi) < 2l_e$, then the diffusivity decreases at low field, and a $\Phi_0$-periodic oscillation dominates the oscillative behavior of the diffusivity, i.e. $D(\tau_\phi, \Phi + \Phi_0) = D(\tau_\phi, \Phi)$ (inset Fig.3). This situation with large mean free path and irrelevance of backscattering indeed leads to a positive magnetoresis-
tance and $\Phi_0$-periodic oscillation, in agreement with the-
tory \[20\]. Whenever $L(\tau_\phi) > 2l_e$, although Aharonov-
Bohm oscillations remain $\Phi_0$-periodic, we get a negative magnetoresistance at low magnetic field, which is consistent with the fact that $\tau_\phi$ is now large enough to allow some backscattering to be efficient. We also remark that the marked reduction of diffusivity which shows up at $\Phi/\Phi_0 = 1/2$ is consistent with a study on small metallic cylinder \[21\].

Case-II (see Fig.4). The case of the incommensurate 2-wall (9,0)@(10,10) is given in Fig.4 (inset) where the power-law diffusion takes place. $\Phi_0$-periodic oscillations and positive magnetoresistance at low field are observed, similar to what is obtained for the ballistic regime in the SWNT case. Conversely, for (6,4)@(10,10)@(17, 13), which present a diffusive-like propagation, there is ev-
hidence for negative magnetoresistance at low field and $\Phi_0/2$-periodicity of $D(\tau_\phi, \Phi)$. The effective elastic mean free path $l_e \simeq 35 \text{ nm}$ (see above), turns out to be larger than the outer shell circumference ($\simeq 7 \text{nm}$). Even in this situation, a small $\Phi_0/2$-periodic oscillation is observed for large $\tau_\phi$. By taking an enhanced value of the coupling pa-
parameter \((\beta = \gamma_0)\), the diffusive regime is reached more rapidly, \(l_\perp \sim 2mn < C\), and together with a negative magnetoresistance at low field, a stronger \(\Phi_0/2\)-periodic oscillation is obtained. These results confirm that magnetotransport properties of MWNTs are very sensitive to the geometry, the number of shells carrying current, and the hamiltonian parameters.

Note that in disordered systems, the basic scheme is that of ballistic electrons scattering on random impurities. The \(\Phi_0/2\) periodicity results from quantum interferences of the electronic pathways around the cylinder wrist. This scheme is not strictly applicable in the case of the incommensurate MWNTs, which means that a clear theoretical understanding of the \(\Phi_0/2\) periodicity has still to be developed, although it is obvious that the diffusive-like regime propagation plays a central role.

**Conclusions.** The above results demonstrate that the behavior observed by Bachtold et al.\(^4\) can be reproduced by considering only the effect of incommensurability. In a real experiment with uniform magnetic field, the flux through a given shell is proportional to its section, whereas here we have taken identical flux for all shells. Our hypothesis is relevant if, in the experimental conditions, the current is confined on a few shells close to the outer one of the MWNT. This confinement could stem from the fact electrons can not go through semiconducting shells, that represent statistically 2/3 of the shells. Note that in the interpretation developed by Bachtold et al., and according to the above results (case-I), the mean free path induced by disorder has to be smaller than the circumference of the nanotube in order to recover the \(\Phi_0/2\) periodicity. Yet, using the formula of White and Todorov\(^3\) with the same disorder parameter, the mean free path is four orders of magnitude larger than the circumference of the outer nanotube, in the experiment of Bachtold et al.\(^4\).

In summary it has been shown that in MWNTs, the electron wavepacket can spread over several shells, due to interlayer coupling. When the ratio between the different shells periodicities along the nanotube axis is irrational, the MWNTs are incommensurate systems. In such a situation, the electronic propagation is not ballistic but depends very much on the geometry and number of shells participating to transport. It has been shown that incommensurability offers an alternative explanation of the experimental results of Bachtold et al.\(^4\) on magnetoresistance, without assuming strong disorder.

MWNTs could provide an unique opportunity of investigating transport in incommensurate quasi one-dimensional conducting systems.

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**FIG. 4.** \(D(\tau_\phi, \Phi)\) (in \(\lambda^2 \gamma_0/\hbar\) unit) of the incommensurate 3-wall (main frame), at time \(\tau_\phi = 3000\hbar/\gamma_0\) for \(\beta = \gamma_0/3\) (upper curve, right y-axis), and at time \(\tau_\phi = 1200\hbar/\gamma_0\) for \(\beta = \gamma_0\) (lower curve, left y-axis). Inset: Same quantity for the 2-wall at \(\tau_\phi = 1200\hbar/\gamma_0\).