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Conduction mechanisms and magnetotransport in multiwalled carbon nanotubes

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We report on a numerical study of quantum diffusion over μm lengths in defect-free multiwalled nanotubes. The intershell coupling allows the wave packet spreading over several shells, and when their periodicities along the nanotube axis are incommensurate, electronic propagation is shown to follow a nonballistic law if a sufficient number of shells are involved in conduction. This results in magnetotransport properties which are exceptional for a disorder free system.

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I. INTRODUCTION

Carbon nanotubes are remarkable for their structure and electronic properties, and seem promising for molecular electronic devices.[1–3] Single-walled 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] Disorder in these systems is very weak leading to mean free path in the μm range.[5]

Multiwalled nanotubes (MWNTs) have a complex structure that consists of several coaxial shells. Their electronic properties are complicated and less understood.[6] Indications for ballistic transport have been reported in some MWNTs,[7] but the interpretation of quantized conductance $n(2e^2/h)$ with half-integer values of n is controversial. Some authors propose an effect of contact between electrode and the nanotube[8] whereas others show that transport through several shells is essential.[9] Many evidences for diffusive regime and quantum interferences effects are also found in other experiments.[4,10,11] This has been interpreted as a result of scattering by structural or chemical disorder, with a mean free path which 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 the following: how many shells contribute to transport, is it just the outer shell that carries current or are inner shells important? Is electronic transport always ballistic in the defect-free MWNTs?

In this paper, we report a theoretical study of quantum diffusion on the μ-meter scale for *disorder-free* MWNTs. The effect of the interlayer coupling on the propagation of the wave packets is analyzed. When the different shells periodicities along the nanotube axis are, incommensurate, the system probed by the electron is not periodic, and we show that this yields *intrinsic* nonballistic transport if sufficient number of shells participate in conduction. 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 $\Phi_0/2$ ($\Phi_0=hc/e$ is 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 $p_\perp$-orbital per carbon atom is kept, with zero onsite energies, whereas constant nearest-neighbor hopping on each layer n (nn), and hopping between neighboring layers (nl) are defined by[12]

$$\mathcal{H}=\gamma_0\left[\sum_{i,j\ \text{n.n.}}|p_\perp^j\rangle\langle p_\perp^i|\right]-\beta\left[\sum_{i,j\in n.l.}\cos(\theta_{ij})e^{(d_{ij}-a)/\delta}|p_\perp^j\rangle\langle p_\perp^i|\right]$$

where θ_{ij} is the angle between the $p_\perp^i$ and $p_\perp^j$ orbitals, and d_{ij} denotes their relative distance. The parameters used here are $\gamma_0=2.9$ eV, $a=3.34$ Å, and $\delta=0.45$ Å.[12] In this tight-binding approach, the differences between SWNTs and MWNTs stem from the parameter β, as the limit $\beta=0$ corresponds to uncoupled shells. An estimate gives $\beta\simeq\gamma_0/8$,[12] but in order to get insight into the effect of β on transport properties, the cases $0\leqslant\beta\leqslant\gamma_0$ have been considered. Synthetized MWNTs contain typically a few tenths of inner layers but due to computer limitations, we have restricted our study to two- and three-wall nanotubes, taking the intershell distance of 3.4 Å as in graphite.

By means of a powerful O(N) method based on a development of the operator $\exp(-iHt/\hbar)$ in a basis of orthogonal polynomials,[13] the time-dependent Schrödinger equation for the evolution of wave packets (WPs) $|\psi\rangle$ up to large time, is solved. This allows us to calculate the spreading of the WPs, defined as $L_\psi(t)=\{\langle\psi|[\hat{X}(t)-\hat{X}(0)]^2|\psi\rangle\}^{1/2}$ over micron length scales [$\hat{X}(t)$ 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 τ_ϕ the electronic wave function looses its phase memory due to some inelastic scattering. The diffusion coefficient at τ_ϕ is also connected to the Kubo conductivity $\sigma=(e^2/h)\rho\langle D(\tau_\phi)\rangle$, where ρ is the density of states, and

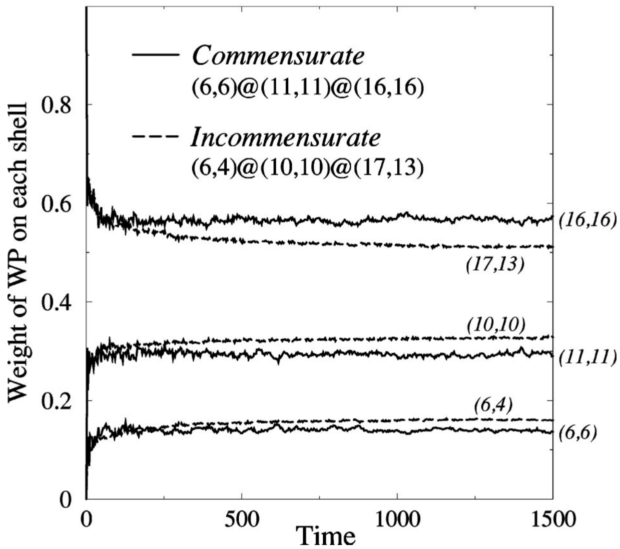

FIG. 1. Temporal repartition of the wave packet over the three shells. The initial state is localized on the outer shell [(16, 16) or (17, 13)]. Time is in $\hbar/\gamma_0$ units and $\beta=\gamma_0/3$.

$\langle D(\tau_\phi)\rangle$ the average of diffusion coefficients for WP close to the Fermi level.[14] The wave packets $|\psi\rangle$ 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 $L(t)=\sqrt{\langle L_\psi^2(t)\rangle}=\sqrt{tD(t)}$, where $\langle\ \ \rangle$ denotes an average over many wave packets. This provides a good qualitative picture of wave packet 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 two per metallic layer.[16]

An essential geometrical observation is that depending on their helicities (n,m), two shells of a given MWNT are commensurate (respectively incommensurate), if the ratio between their respective unit cell lengths $T_{(n,m)}$ along the tube axis is a rational (respectively irrational) number.[2] 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 pure 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 $a_{cc}=1.42$ 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 $T_{(17,13)}=3\sqrt{679}a_{cc}$).

II. 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).

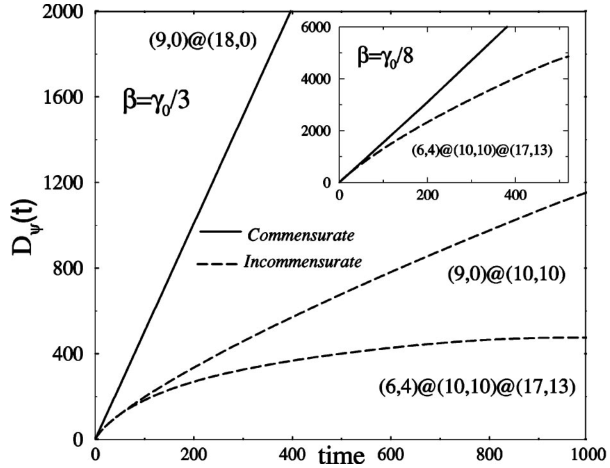

FIG. 2. Main frame: Diffusion coefficients for typical two-wall and three-wall commensurate and incommensurate MWNTs (for $\beta=\gamma_0/3$) as a function of propagation time (in $\hbar/\gamma_0$ units). Inset: Same quantity for the (6,4)@(10,10)@(17,13) with $\beta=\gamma_0/8$.

Only two representative cases of three-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 $\tau_{ll}\sim\hbar\gamma_0/\beta^2$, in good agreement with the Fermi Golden Rule. By changing the amplitude of β in the range $[\gamma_0/8,\gamma_0]$, the expected scaling form of τ_{ll} is checked. Note that for two electrodes separated by 1 μm and assuming ballistic transport with a Fermi velocity of 10^6 ms^{-1}, the corresponding time is $t\sim 4500\hbar/\gamma_0$. This is two orders of magnitude larger than τ_{ll} (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.

III. 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 $v\simeq 5\times 10^5$ ms^{-1}, deduced numerically, is close to the averaged Fermi velocity of one isolated shell. It is nearly independent on β and depends weakly of the shells constituting the MWNT.

In the two-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 environnements.[13,17]

In the three-wall incommensurate systems, a saturation of the diffusion coefficient is seen at large time, which is equivalent to a diffusivelike behavior ($L(t)\sim\sqrt{t}$) as observed in disordered systems. This allows to define an effective mean free path $\tilde{l}_e$ and an effective scattering time $\tilde{\tau}_e$

from $\lim_{t\to\infty} D(t)=D_0=\tilde{l}_e v=v^2\tilde{\tau}_e$, where v^2 is the slope of $D(t)$ at origin. One can estimates an effective elastic mean free path $\tilde{l}_e \simeq 35$ nm for $\beta=\gamma_0/3$ (Fig. 2).

The striking difference between the two-wall and three-wall incommensurate cases, with the same Hamiltonian parameters β and γ_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 contributing to conduction. Contrary to the case of commensurate systems, in which the quantum diffusion through several shells is ballistic (for all β), the diffusion law in incommensurate MWNTs is sensitive to the value of β. For example, for β varying between $\gamma_0/3$ and γ_0, the diffusion exponent for the two-wall varies between $\eta=0.88$ and $\eta=0.75$, and the estimated mean free path for the three-wall incommensurate system varies between 35 nm and 2 nm. For $\beta=\gamma_0/8$, the diffusive regime in the three-wall is not reached in the evolution time accessible to the computation (inset of Fig. 2).

IV. 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.[14] They correlate this effect to an intrinsic disorder and assume that the current is carried only by the outermost shell.

In order to analyze the origin of these experimental results, we compare two scenarios. 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 introduced by a random modulation of onsite energies in the range $[-V_d/2, V_d/2]$, in order to tune the value of the mean free path, since $l_e \propto 1/V_d^2$ in the limit of weak scattering.[5,19] 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 $e^{i\varphi_{ij}}$ with $\varphi_{ij}=e/h\int_i^j \mathbf{A}\,d\mathbf{r}$, where $\mathbf{A}$ is the vector potential. We look at $D(\tau_\phi,\Phi)$, where Φ is the flux of the magnetic field through the tubes taken identical for all tubes. It is sufficient to consider $0<\Phi<\Phi_0$ since at least a Φ_0 periodicity is expected from gauge invariance.[18] We assume that variations of the diffusivity give the main contribution to magnetoconductance.

V. CASE I

Several types of situations occur depending on the relative values of $L(\tau_\phi)$, l_e, and $\mathcal{C}$, which are respectively the average spatial extension of WP at the time τ_ϕ, the elastic mean free path, and the circumference of the nanotube (see Fig. 3). 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 τ_ϕ, two different behaviors are obtained. If $L(\tau_\phi)<2l_e$, then the diffusivity decreases at low field, and a Φ_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 magnetoresistance and Φ_0 periodic oscillation, in agreement with theory.[19] Whenever $L(\tau_\phi)>2l_e$, although Aharonov-Bohm oscillations remain Φ_0 periodic, we get a negative magnetoresistance at low magnetic field, which is consistent with the fact that τ_ϕ 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.[20]

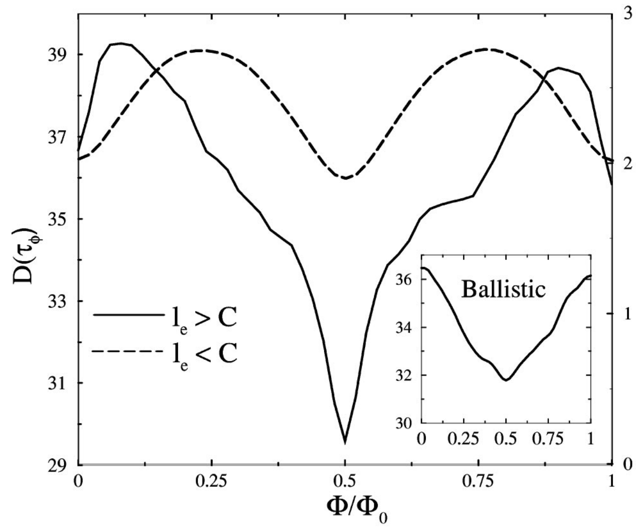

FIG. 3. Main frame: $D(\tau_\phi,\Phi)$ (in $\text{Å}^2\gamma_0/\hbar$ unit) for a metallic SWNT (9,0) evaluated at time $\tau_\phi \gg \tau_e$, for two disorder strengths, $V_d/\gamma_0=3$ and 1, such that the mean free path ($l_e\sim 0.5$ and 3 nm, respectively) is either shorter (dashed line) or larger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

VI. CASE II

The case of the incommensurate two-wall (9,0)@(10,10) is given in Fig. 4 (inset) where the power-law diffusion takes place. Φ_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 presents a diffusivelike propagation, there is evidence for negative magnetoresistance at low field and $\Phi_0/2$ periodicity of $D(\tau_\phi,\Phi)$. The effective elastic mean free path $\tilde{l}_e\simeq 35$ nm (see above), turns out to be larger than the outer shell circumference ($\simeq 7$ nm). Even in this situation, a small $\Phi_0/2$ periodic oscillation is observed for large τ_ϕ. By taking an enhanced

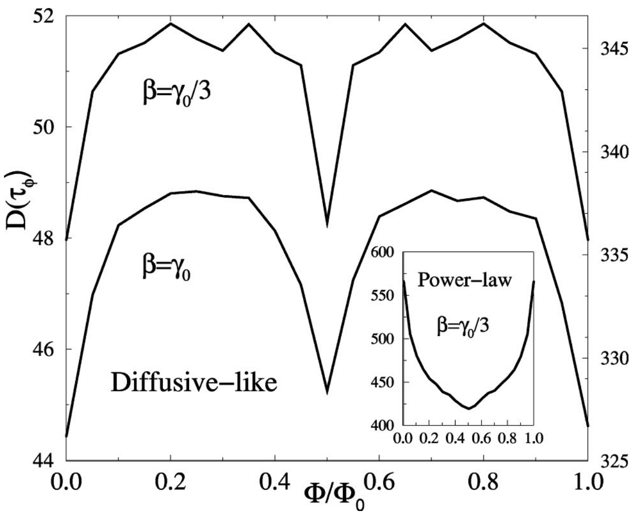

FIG. 4. $D(\tau_\phi,\Phi)$ (in $\AA^2\gamma_0/\hbar$ unit) of the incommensurate three-wall (main frame), at time $\tau_\phi=3000\hbar/\gamma_0$ for $\beta=\gamma_0/3$ (upper curve, right y axis), and at time $\tau_\phi=1200\hbar/\gamma_0$ for $\beta=\gamma_0$ (lower curve, left y axis). Inset: Same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

value of the coupling parameter ($\beta=\gamma_0$), the diffusive regime is reached more rapidly, $\tilde{l}_e\sim 2$ nm$<\mathcal{C}$, 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 propagation regime plays a central role.

VII. CONCLUSIONS

The above results demonstrate that the behavior observed by Bachtold *et al.*[11] can also be reproduced by considering only the effect of incommensurability. In a real experiment with uniform magnetic field, the flux through a given shell is proportionnal 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 layers close to the outermost shell of the MWNT. This confinment could stem from the fact that 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[5] with the same disorder parameter, the theoretical mean free path in the experiment of Bachtold *et al.*[11] should be four orders of magnitude larger than the circumference of the outer shell.

In summary, the intrinsic geometry of MWNTs (helicity and number of individual shells) is an important factor to determine the resulting electronic wave packets propagation in disorder-free systems, especially for chemical potential away from the charge neutrality point.

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