Anomalous diffusion and elastic mean free path in disorder-free multi-walled carbon nanotubes

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We explore the nature of anomalous diffusion of wave packets in disorder-free incommensurate multi-walled carbon nanotubes. The spectrum-averaged diffusion exponent is obtained by calculating the multifractal dimension of the energy spectrum. Depending on the shell chirality, the exponent is found to lie within the range $1/2 \leq \eta < 1$. For large unit cell mismatch between incommensurate shells, $\eta$ approaches the value $1/2$ for diffusive motion. The energy-dependent quantum spreading reveals a complex density-of-states-dependent pattern with ballistic, super-diffusive or diffusive character.

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The understanding of charge transport in structurally clean systems, with complex and aperiodic long-range correlations, has been the subject of intense debate during the past two decades [1]. The quantum dynamics in most of these systems has been described as an anomalous quantum diffusion process, related to the multifractal nature of the electronic states and spectra [2]. These unconventional transport mechanisms are incompatible with a dominant transport length scale such as the elastic mean free path, and the occurrence of a diffusive regime. Recently, the discovery of carbon nanotubes has provided a whole class of new quasi-one-dimensional systems with spectacular effects of topological arrangements of carbon atoms on the electronic spectra [3,4]. The multi-walled nanotubes (MWNTs) are intrinsic incommensurate objects since, due to registry mismatch between neighboring shells, there are very few cases in which the respective symmetries of individual shells allow finding a common unit cell for the whole object. In most cases, the unit cell length (along the nanotube axis) ratio between adjacent shells is an irrational number, and the MWNT taken as a whole becomes an incommensurate object [5]. In recent years, mechanical [6] and electronic [7,8,9,10,11,12] properties of double- and triple-walled incommensurate nanotubes (i-DWNTs and i-TWNTs, respectively) have been intensively investigated. Roche et al. [6] first reported on anomalous diffusion properties of i-DWNTs and i-TWNTs by numerical analysis of the wave-packet propagation. Signatures of anomalous diffusion were further inferred by the evaluation of the energy spacing distribution of energy levels [2], exhibiting Wigner-Dyson, Poisson and semi-Poissonian statistics depending on the position of the Fermi level. In a recent work [11], the existence of a finite (energy-dependent) elastic scattering rate for electrons in the outer shell of a disorder-free i-DWNTs was analytically shown to be a consequence of helicity-determined selection rules for inter-shell tunneling [2,12].

Aim of this letter, is to establish the connection between spectral and clarify the dynamical properties of i-DWNTs, i-TWNTs and in general MWNTs. Our results provide a deeper insight on why, experimentally, MWNTs typically, but not always [13,14] exhibit normal diffusion behavior, with an energy dependent mean free path [15]. However, we predict global anomalous diffusive behavior in i-DWNTs and in many i-TWNT systems. To this extend, first we calculate the spectrum-averaged diffusion exponent $\eta$, which describes the spread in time of an initially localized wave packet by looking at the mean square displacement

$$X^2(t) \simeq t^{2\eta}. \quad (1)$$

For this we evaluate the multifractal dimension $1/2 \leq D_{-1} < 1$ of the energy spectrum of various incommensurate, tunnel coupled, i-DWNTs and i-TWNTs, and use the relation $\eta = D_{-1}$ [16,17]. We find a good agreement with previous calculations using a wave-packet propagation approach [15]. We find that the exponent $\eta$ strongly depends on the chirality and on the number of shells. In particular, for fixed number of shells, e.g. two, one can find that $\eta$ is closer to the value $1/2$, characteristic of normal diffusion, if at least one shell has a large unit cell. Also upon increasing the number of shells the diffusive limit $1/2$ is more rapidly approached. For example, for the i-TWNT $(6,4)@(17,0)@(15,15)$ is already $\eta \simeq 1/2$ such that for such a tube some elastic mean free path can be extracted from the wave-packet evolution. In contrast, for the $(5,5)@(17,0)@(15,15)$ i-TWNT, with a very small unit cell of the $(5,5)$ shell, the diffusion remains anomalous, and thus no global mean free path can be extracted. While the exponent $\eta$ describes spectrum-averaged properties, more information about the interplay between density of states and degree of anomaly can be extracted from the energy dependent quantities.
Thus wave-packet spreading is investigated by solving the
time-dependent Schrödinger equation and calculating the
energy-dependent quantum spreading
\[ \ell(E, t) = \frac{X^2(E, t)}{v(E)t} \equiv \frac{\text{Tr}\{\delta(E - \hat{H})(\hat{X}(t) - \hat{X}(0))\}^2}{\text{Tr}\{\delta(E - \hat{H})\} v(E)t}. \]

Here \( \delta(E - \hat{H}) \) is the spectral measure operator, whose
trace gives the total density of states \( n(E) \), \( \hat{H} \) is the
system’s Hamiltonian, and \( \hat{X}(t) \) is the position operator
along the tube axis. Finally, \( v(E) \) is the group velocity
at energy \( E \). In some situations \( \ell(E, t) \) becomes time-
independent such that energy-dependent elastic mean
free path is can be defined even if the global exponent \( \eta \) is not 1/2!

Our starting model to evaluate wave-packet spreading is the
tight-binding Hamiltonian for a MWNT with \( M \) shells,
where only one \( p_{\perp} \)-orbital per carbon atom is kept,
and with zero on-site energies. With a nearest-neighbor
hopping \( \gamma_0 \) on each layer \( n \), and hopping \( \beta \) between
neighboring layers, it has the form \[ \hat{H} = \gamma_0 \sum_{n=1}^{M} \sum_{\langle i,j \rangle} |p_{\perp,i}^{n}\rangle \langle p_{\perp,i}^{n}| - \beta \sum_{\langle n,m \rangle} \sum_{i,j} \cos(\theta_{ij}) e^{-d_{ij}/a} |p_{\perp,i}^{n}\rangle \langle p_{\perp,j}^{m}|, \]
where \( \langle n,m \rangle \) and \( \langle i,j \rangle \) are sums over nearest shells and
nearest neighboring atoms, respectively. Moreover, \( \theta_{ij} \) 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:
\( \gamma_0 = 2.9 \text{ eV}, a = 3.34 \ \text{Å}, \delta = 0.45 \ \text{Å} \). An ab-initio
estimate gives for the intershell coupling \( \beta \approx \gamma_0/8 \).
Starting from Eq. \[ \ell \], the spreading of wave packets is
now evaluated along different routes. For our first approach,
we start by observing that the dynamics of wave packets in a system is strongly related to the properties of
the system’s energy spectrum. The latter can be generally
divided into absolutely continuous, singular contin-
uous and pure point parts \[ \hat{H} \]. The wave packets spread
ballistically if the energy spectrum is absolutely contin-
uous and are localized in systems with purely point-like
spectra. If the spectrum is singular continuous the wave
packets anomalously spread \[ \hat{H} \]. The singular continuous
spectrum is a multifractal object which can be characterized by
each of a set of fractal dimensions \( D_q \). Piféchon has shown that, at large times \( t \to \infty \), the
moments spread as \( X^q(t) \sim t^{D_{1-q}} \), with \( D_q \) the fractal
dimension of the energy spectrum \[ \hat{H} \]. Then, the spreading
of a wave packet is determined by \( D_{-1} \). The motion of wave packets in a system with singular continuous
energy spectrum will be normal diffusive if \( D_{-1} = 1/2 \), or
anomalous diffusive if \( 1/2 < D_{-1} < 1 \). The energy spec-
trum of an incommensurate system is usually singular
continuous, or maintain intrinsic self-similar features \[ \hat{H} \].
Therefore, one may expect some anomalous diffusive be-
behavior of wave packets in i-DWNTs. In order to calculate
the energy spectrum of an i-DWNT, we approximate the
irrational ratio of the unit cell lengths of the inner and
outer shells by one of its convergents, which is the ration-
numeral obtained by truncating the continued fraction
representation of the given irrational number up to a cer-
tain term \[ \hat{H} \]. That is, we approximate the i-DWNT
by a commensurate DWNT. As the chosen convergent
becomes closer to the irrational unit cell ratio, the energy
spectrum of the commensurate DWNT gets closer to
that of the i-DWNT under study. We calculate the
energy spectrum of the commensurate DWNT by direct
diagonalization of the Hamiltonian in Eq. \[ \hat{H} \]. After comp-
uting the energy spectrum, we count the numbers of
boxes \( N(l) \) with length \( l = \Delta E/2^n \) needed to cover it.
Here \( \Delta E \) is the range of the energy spectrum and \( n \) is a positive integer. Thus, the probability density \( p_i(l) \) is obtained
for each box by calculating the ratio of the number of
points falling into the box \( \Lambda_i(l) \) to the total number of
points in the data. The set of fractal dimensions \( D_q \) can be
defined as
\[ \sum_{i=1}^{N(l)} p_i^{q+1}(l) \sim l^{D_{q+1}}, \quad \text{as } l \to 0. \]

For a simple fractal object, that is, the probability den-
sity \( p_i(l) \) is the same for each box \( \Lambda_i(l) \), all general di-
mentioned defined above have the same values \( D_F \). In
this case, the probability density is \( p_i(l) = 1/N(l) \), with
\( N(l) \sim l^{-D_F} \). Therefore is \( D_{q+1} = D_F \) for any \( q \). Here,
\( D_F \) is the fractal (box-counting) dimension. In general,
the distribution of points in a fractal object is different
different boxes. That is, the probabilities of finding a
point in the different boxes are different. If \( q = -1 \), one
has \( D_0 = D_F \). For \( q = -2 \) the dimension \( D_{-1} \) can be
calculated by
\[ D_{-1} = \frac{1}{2} \lim_{l \to 0} \frac{\ln \sum_{i=1}^{N(l)} p_i^{-1}(l)}{\ln l}. \]

Hence, the dimension \( D_{-1} \) is extracted from a linear re-
gression fit to the plot of \( A_q \equiv -\frac{1}{2} \ln \sum_{i=1}^{N(l)} p_i^{-1}(l) \) as a
function of \( \ln l \). As an example, Fig. \[ \hat{H} \] shows results for
the energy spectrum of the i-DWNT \( (9,0)(10,10) \). As
discussed in Ref. \[ \hat{H} \], the incommensurability of the
two unit cells yields a non-vanishing intershell tunnel-
ning only when helicity-determined selection rules are ful-
filled, which can occur only if enough sub-bands in each
shell become populated. In turn, this yields a finite
lifetime for electrons in one shell due to effective back-
scattering processes. Here we show that these features
are also reflected in the energy spectrum which, as shown
in Fig. \[ \hat{H} \] exhibits a fractal character. We find that within
the energy range \([-12.664 \text{ eV}, 12.898 \text{ eV}] \) the fractal di-
sension converges to the value \( \eta = 0.88 \), when the
incommensurate ratio \( T_{(10,10)}/T_{(9,0)} = 1/\sqrt{3} \) is approxi-
mated by the 6th convergent 15/26 obtained by truncating the continued fraction expression of $1/\sqrt{3}$. This value is the same as found from numerical wave-packet propagation of initially localized wave packets [2]. Here, $T_{(n,m)} = a_0 \sqrt{3(n^2 + nm + m^2)}/\text{GCD}$ is the length of the axial unit cell of shell $(n,m)$, with the carbon-carbon bond length $a_0$ and GCD being the greatest common divisor of $(2n+m)$ and $(m+2n)$.

In order to understand the role of chirality, we have also investigated the cases of the $(6,4)@\langle17,0\rangle$ and $(5,5)@\langle17,0\rangle$ i-DWNTs, differing in the chirality of the inner shell. One has $T_{\langle17,0\rangle}/T_{\langle5,5\rangle} = \sqrt{3}$, while $T_{\langle17,0\rangle}/T_{\langle6,4\rangle} = 1/\sqrt{19}$. The difference in the two exponents is noticeable: $\eta_{\langle5,5\rangle}@\langle17,0\rangle \approx 0.88$ and $\eta_{\langle6,4\rangle}@\langle17,0\rangle \approx 0.82$. We attribute the smaller exponent of the $(6,4)@\langle17,0\rangle$ i-DWNT compared to that of the $(5,5)@\langle17,0\rangle$ i-DWNT to the larger unit shell mismatch. Having in mind the i-DWNT $(5,5)@\langle17,0\rangle$, we add an additional outer shell and consider the i-TWNTs $(5,5)@\langle17,0\rangle@\langle15,15\rangle$ and $(6,4)@\langle17,0\rangle@\langle15,15\rangle$. For the first TWNT the diffusion is still anomalous with $\eta_{\langle5,5\rangle}@\langle17,0\rangle@\langle15,15\rangle \approx 0.88$, however. The effect of the additional armchair shell (15,15) is to randomize the energy spectrum of the $(6,4)@\langle17,0\rangle@\langle15,15\rangle$. To be definite, already for the approximation 26 : 26 : 15 to the ratios $3\sqrt{19} : 3 : \sqrt{3}$ we find the value $\eta \approx 0.60$, as shown in Fig. 2. Notice that, since $D_{-1}$ is defined in the limit of box length $l \to 0$, for the linear fit in Fig. 2 the five points corresponding to the smallest lengths $l$ have been considered.

As second calculation route, the energy-dependent and time-dependent wave-packet spreading $\ell(E,t)$ is analyzed numerically. The resolution of the time-dependent Schrödinger equation is made by expanding the evolution operator $e^{-i\hat{H}t}$ on a basis of orthogonal polynomials. This method has been demonstrated to provide an efficient real-space computational framework for an order $N$ algorithm [23]. The total length of the MWNTs is finite but several tens of $\mu\text{m}$-long in order to limit boundary effects. For example, the calculations shown in Figs. 8 and 4 are performed with a finite length of about $24\mu\text{m}$, whereas the unit time step is taken as $T = 14h/\gamma_0 \approx 3.18$ fs. Most generally, the anomalous quantum spreading is driven by a time dependent power law, $\ell(E,t) = t^{\eta(E) - 1}/\nu(E)$, whose asymptotic regime gives the conduction regime. When $\ell(E,t)$ tends to some
finite constant at large times, some energy-local elastic mean free path \( \ell_{el}(E) \) can be extrapolated as \( \ell_{el}(E) = \lim_{t \to \infty} \langle E, t \rangle \). In Fig. 3 and Fig. 4 (main frame), the energy-dependent length scale \( \ell(E, t) \) is shown at several chosen elapsed times \( t \), starting from wave packets that are homogeneously spread in real space with random phase on each lattice point.

For the case of \( (9, 0)@((10, 10) \) (Fig. 3), and energies in the charge neutrality point vicinity, a careful analysis of propagation over several tens of microns reveals no deviation from a ballistic-like regime with \( \eta(E) = 1 \). Conversely for a small energy window in a high density of states region, a very slowly varying length is observed. Here the effect of incommensurability becomes more pronounced due to the enlarged electronic population available for scattering. The result of the energy-averaged diffusion exponent gives the global exponent \( \eta = 0.88 \) intermediate between the value 1 and 1/2, and in agreement with prior analysis.

In the case of stronger incommensurate systems, such as the \( (6, 4)@((17, 0)@((15, 15) \) i-TWNT, the tendency towards energy-dependent anomalous conduction becomes even more pronounced. First the region of 2 eV around the charge neutrality point remains almost ballistic, whereas the rest of the electronic spectrum shows a very slower expansion of wave packet in time. The propagation time runs from 0.4 ps \( (t = 2000T) \) to 1.5 ps \( (t = 6710T) \), and clearly \( \ell(E, t) \) either shows anomalously slow diffusion, or saturates at very short times (inset in Fig. 4). Whenever the saturation limit is clearly reached, a mean free path \( \ell_{el}(E) \) for the whole object can be meaningfully extracted. \( \ell_{el} \) is found to be around 200 nm to 400 nm for energies in between 2 eV to 3.5 eV.

To conclude, we found that the energy-averaged exponent \( \eta \) depends crucially on chirality and number of coupled shells with global anomalous behavior strongly pronounced in i-DWNT. When looking to energy-dependent properties, we found that even for i-MWNT exhibiting \( \eta(E) \sim 1 \) (ballistic spreading) close to the charge neutrality point, some elastic mean free path can be defined in regions of larger density of states where \( \eta(E) \sim 1/2 \).

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