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Quantized conductance of multiwalled carbon nanotubes

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We report calculations of the transport properties of multiwalled carbon nanotubes based on a scattering-theoretic approach that takes into account scattering within each tube, between tubes, and at the metal contacts. We find that only the outer tube contributes to the conductance, as has been implied by experiments. Referring to experiments performed with liquid-metal contacts, we also explain why the measured conductance is close to an integer number of conductance quanta, when the tubes are immersed in the liquid metal for several hundreds of nanometers and is not an integer when they are immersed for only a few nanometers. Finally, we propose that the observed conductance of only one quantum (instead of the expected two quanta) is due to intertube interactions. © *1999 American Institute of Physics.* [S0003-6951(99)03650-5]

Single and multiwalled carbon nanotubes (MWNTs) have attracted considerable experimental and theoretical interest since they were first studied by Iijima in 1991.[1] In the last year, several groups have reported conductance measurements of individual tubes under various types of contacts.[2–4] In particular, the data reported by de Heer and co-workers[2] revealed puzzling features for which a theoretical explanation is lacking. The data show that electron transport in these nearly perfect structures is ballistic. Within the Landauer formalism,[5] we then expect the conductance of a nanotube to be determined by the number of Fermi-level conducting channels and the transmission factors T_i for each channel: explicitly,

$$\sigma=\sum_{i=1}^{M} T_i \frac{2e^2}{h}=\sum_{i=1}^{M} T_i G_0, \tag{1}$$

where $G_0=1/12.9\ \mathrm{k}\Omega$ is the quantum of conductance, and the sum runs over the M available quantum channels. The T_i are the transmission factors of each channel, with $0\leqslant T_i \leqslant 1$. For the important (n,n) armchair nanotubes which are metallic, there are two p_z-derived bands at the Fermi level, one even and one odd under the n axial mirror symmetries of the tube, and so, one expects that a single armchair nanotube has a conductance of $(T_e+T_o)G_0$, where T_e, T_o are the transmission coefficients of these even and odd bands, respectively. If the transmission coefficients are unity, we then get a conductance of $2G_0$ at the Fermi level. For the case of a MWNT composed of m individual tubes, each having two channels at the Fermi level, the maximum ballistic conductance is thus $2mG_0$. However, the data of de Heer and co-workers[2] indicate clearly that only one tube in a MWNT contributes to the conductance. In this experiment one end of a MWNT was immersed in a liquid metal, with the other end in contact with a graphitic fiber. This experiment has also shown that, unlike the expected conductance of $2G_0$ (assuming only the outermost tube conducts), the conductance of the MWNT is G_0 when the tube is immersed in the liquid metal for several hundred nanometers and a fraction of G_0 when only the tip of the MWNT (around 30 nm) is in the liquid.

In this letter, we consider the puzzling results of the above experiments and set up a model of a multiwalled nanotube composed of armchair tubes to show that only the outermost tube gives rise to conduction, as is indeed observed. We then consider the issue of the numerical value of the transmission coefficient for any open channel: this is not necessarily unity and should, in principle, depend sensitively on the details of the contacts. We suggest, however, that saturation and decoherence effects associated with the liquid-metal contacts give rise to a transmission of unity for any open channel. This result applies also to many other contact geometries used in transport experiments[6] and is thus of general validity.

We describe the scattering properties of a finite-length MWNT by placing at each C site a potential with two properties: it acts as a splitter[7] for the propagating electron wave function with three channels for in-tube scattering (along the sp^2 bonds) and two channels for intertube scattering (one above and one below the tube), and it contains a single bound state that captures the physics of the p_z-derived π and π^* Fermi-level bands. The $C-C$ distance, which governs the decay in the wave function as it propagates along the bonds, has been fixed to the experimental value of 1.42 Å. The single-splitter bound-state energy is fixed in such a way that the band structure of a single *infinite* nanotube is correctly reproduced in the vicinity of the Fermi level, which is the energy region of interest in our problem. The MWNT is formed by putting m (n,n) nanotubes inside each other and connecting the vertical connections of the splitters in the appropriate way. This is the simplest possible type of MWNT where all the tubes have the same indices and are aligned exactly with each other. A schematic picture of a MWNT composed of two tubes is presented in Fig. 1. We terminate the MWNT at each end by connecting each of the $2n$ outward-pointing scattering connections on the outermost nanotube to a potential step, which models the presence of the contact on the outermost tube. We follow the method outlined in Ref. 7 to generate the scattering matrix of the

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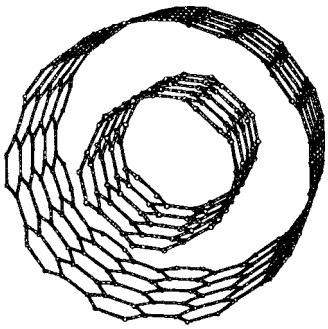

FIG. 1. Schematic view of a multiwalled nanotube formed from two tubes.

single splitter and then of the entire network. Using this $4n \times 4n$ matrix, we calculate the transmission coefficients of the network at any given energy. The conductance is then calculated according to Eq. (1). Other details of the calculations will be given elsewhere.[8]

We first note that with this model we reproduce some known results for single-tube transport: for the simplest case of a perfect nanotube we find, as expected, two channels at the Fermi level, with a maximum conductance of $2G_0$.[9] With a single vacancy present one channel is lost,[9] and with an axial magnetic field present an Aharonov–Bohm effect is seen where the resistance varies periodically with the number of flux quanta through the tube.[10] The model is thus robust enough to investigate the effects.

Only the outermost tube conducts. The experiments of Refs. 2 and 11 strongly suggest that only a few, or possibly one, of the nanotubes in a MWNT contribute to the conductance. Indeed, with our model we confirm that the presence of the other tubes in the MWNT does not affect the overall conductance significantly. The current is injected into the outermost tube of the MWNT, as in the experiments, but even with m tubes present we found only two open channels at the Fermi level, yielding a maximum conductance of $2G_0$. We note that, due to the intertube interaction, the states of one tube mix with those of another to form the eigenstates of the composite system. In this way, the states of the inner tubes, and therefore their conductance channels, should be present on the outermost nanotube, and so leak to the contacts, suggesting an increase of conductance. However, only the local density of states (LDOS) at the position where the electrons are injected is important for determining the conductance, and the LDOS on the outermost tube is not changed even if the electrons delocalize from tube to tube.[12] Furthermore, the single-nanotube wave functions at the Fermi level decay very quickly away from the tube surfaces. The work function for graphite is about 4.7 eV,[13] which corresponds to a wave-function decay constant of 0.9 Å. If we assume exponential behavior to be valid 1 Å outside the surface of the tube, within a tube–tube distance of 3.5 Å the wave function has decayed to 25% of its initial value. Once we include the three-dimensional nature of the Schrödinger equation, however, a much larger decay rate is predicted.[14] The decay constant is amplified by the kinetic energy of the electron along the surface of the tube. For graphite, at the Fermi level, the surface oscillations of the wave function correspond to an energy of 11 eV. This effective increase in the work function generates much greater decay, and following the above analysis we now find that between tubes the wave function should have decayed to 5% of its initial value. Thus, the transmission coefficient for propagation from the surface into the inner tubes will be very small on average, even for the tube closest to the outermost tube.

The outermost transmission coefficients are unity. In addition to the scattering inside the tube, our study also includes the reflections that occur when the electron enters and leaves the nanotube via the contacts. We found that the resulting transmission factors depend sensitively on the potential structure in the interface region between the nanotube and the contacts, and so, should be some arbitrary real numbers that would need to be calculated from an *ab initio* approach.[15] On the other hand, de Heer and co-workers[2] have shown that the transmission coefficients turn out to be close to integers. It is hard to reconcile this result with elastic transmission factors as in the Landauer formula (1). Therefore, the question arises as to why the measured conductances are of the form iG_0, where i is an integer, and not of the expected form $i\overline{T}G_0$, where $\overline{T}$ is the average transmission of the available channels which may be much less than 1. The answer lies in the nature of the contacts made to the nanotube, and here we consider both the liquid–tube and the tube–fiber interface.

First, for the contact with the liquid metal, we note that unlike the configuration pictured in the Landauer approach[5] in which the reservoirs are linked to the sample by horn-shaped ballistic conductors, here the nanotube is directly inserted into the reservoir. Two effects tend to enhance the effective transmission and cause it to saturate at one. As we are really in a time-dependent inelastic regime, the transmission coefficient at a given energy for hopping to a particular area of the tube will oscillate with time, due to thermal effects. Also, the more surface area of the nanotube that makes contact with the liquid metal, the more transitions happen per unit time, thus saturating any sufficiently open channel by filling it with electrons. One could think of the liquid as being composed of a series of layers of thickness 10 nm or so, with each layer acting as a separate reservoir, and each making contact with the same nanotube. Each time an electron tunnels into the nanotube the individual probability of tunneling is not just of the form of a transmission as in Landauer's formula (1), but must also include the nonequilibrium distribution function reflecting the occupation of the nanotube mode into which the electron is tunneling. Given sufficiently many (incoherent) opportunities for tunneling into this mode, the latter will eventually be completely filled, and the measured current will be that appropriate to a completely filled mode. This yields an entire quantum of conductance, and so, working backwards from Eq. (1), we deduce an effective transmission factor of 1 for this mode. We call this transmission factor *effective* because it does not come from a calculation for any one particular atomic geometry, but from the cumulative effects of many different geometries, at many different sites on the MWNT surface. We assume here that the exponential decay between the tubes is sufficiently strong to render the LDOS of the inner tubes inaccessible to this saturation mechanism.

As for the other contact, the nanotube is embedded in a graphitic fiber composed of nanotubes and graphitic par-

ticles, connected to a gold wire with silver paint.[2] Thus, there should be many contacts to the nanotube generating many conducting paths leading up to the gold wire. Therefore, in the elastic scattering approach, the effective transmission from the tube to the fiber should be high. The rest of the fiber beyond this immediate contact region has a small resistance: taking the nominal figures given in Ref. 2 and a resistivity of roughly 500 $\mu\Omega$ cm, we calculate a total resistance of 200 Ω for the fiber.[16] This small series resistance might explain why the conductance plateaus observed in Ref. 2 seem to be slightly below integer values.

Now, if there is an elastic scatterer in between the two contacts, the conductance will be reduced according to the Landauer formula (1). The cap–shaft interface between the nanotube tip and the bulk acts as such a scattering center, and the conductance would lower to noninteger values when only the tip is immersed into the liquid metal, as the authors proposed in Ref. 2 to explain their experimental observations. Once this junction is pushed below the surface, its effect on electron transmission is removed and the conductance rises up to the full integer value: the electrons can now tunnel from the liquid metal directly into the bulk of the nanotube.

We conclude the letter by analyzing the last puzzling aspect of the liquid-metal experiment, i.e., the discovery that only one quantum of conductance is measured for the MWNT, and not two. From our arguments above, it is unlikely that this reduction arises from the physics of the liquid–tube interface, as the disorder and high contact area should guarantee that all available conductance channels are filled. However, intertube interactions in ropes can substantially alter the physics of ropes precisely at the Fermi level.[13] These interactions perturb the band structure of the single tubes *significantly* and cause the existing even and odd bands to repel each other, creating a depletion of states at the Fermi level. This effect is similar to that observed in AB graphite, where instead of four bands being present at the Fermi level, only two are found.[13] In graphite, this interlayer interaction reduces the LDOS at the Fermi level by a factor of 1/2 exactly, as the other states that would have completed the LDOS of the graphene sheets have been pushed away in energy from the Fermi level. As long as this repulsion is greater than the small bias voltages used in the experiment, these other states will not be available for transport. A clear picture of this effect can be seen in scanning tunneling microscopy (STM) images of graphite, where exactly one half of the surface atoms are visible at low biases.[17] We thus propose that the intertube interaction, either between the tubes in the MWNT or at the contacts between tubes in the fiber can cause similar band repulsion, reducing the LDOS present precisely at the Fermi level by a factor of 1/2 and thus reducing the number of channels available at this energy from 2 to 1.

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