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Electronic and transport properties of carbon nanotubes $_{\rm Seminar}$

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Abstract

A carbon nanotube (CN) is a graphene sheet rolled into a hollow cylinder with nanometric diameter and with length in the micrometer range. This seminar presents the zone folding approximation for calculating electronic band structure of carbon nanotubes and its limitations. In the second part, it presents the application of Landauer formalism on quasi-onedimensional transport in carbon nanotubes. Experimental confirmation of theoretic models is presented as well.

Contents

1	Introduction	2
2	Synthesis and structure of carbon nanotubes	2
3	Electronic properties of carbon nanotubes	4
4	Electrical transport in single-wall carbon nanotubes	9
5	Conclusion	13

1 Introduction

Carbon nanotubes are closely related to the monolayer of graphite — graphene, a carbon honeycomb lattice (Figure 1). In graphite, monolayers are bound by van der Waals force, not through chemical bonding. The interlayer distance is 0.34 nm, while the length of the carbon-carbon bond is 0.142 nm. Relatively weak bonding between layers is a reason for the graphite's tendency to split. When drawing with a pencil, monolayers of graphite are formed as well as thicker layers. Therefore, producing graphene is not very difficult, though it is hard to observe. It is not visible under an optical or electron microscope. Searching for a monolayer in the cleavage product with atomic force microscopy would be a mission impossible. Only a few years ago, the monolayer was actually observed on a SiO₂ substrate by combining results of different microscopy techniques [1]. This year's Nobel prize was awarded to Geim and Novoselov for this achievement [2]. Graphene itself has many interesting properties. The advances in production, isolation and characterization by Geim and Novoselov contributed to a renewed interest of scientific community into the field. It is also likely that the field of carbon nanotubes will profit from the experimental and theoretical results for graphene.

Carbon nanotube (CN) is a graphene sheet, rolled into a hollow cylinder with nanometric diameter and length in micrometer range. Nanotubes were commonly identified as hollow tubes in the core structure of carbon fibers in the 1970s [3], but their popularity rose drastically after they were observed on the cathode of carbon arc used to produce fullerens in 1991. Carbon nanotubes form spontaneously under well-defined conditions either as single-wall (SWNT, diameter d_t between 0.4 nm and 3 nm) or nested multiwall (MWNT, 1.4 nm $< d_t < 100$ nm) nanotubes. Three main methods for SWNT production are arc discharge, laser ablation and chemical vapor deposition. The mechanism of carbon nanotube growth is not yet understood very good [3].

Nanotubes are regarded as either single molecules or quasi-onedimensional crystals [4]. Onedimensional systems have interesting properties that normally cannot be found in our three-dimensional world, and have been studied for decades before discovery of nanotubes. Nanotubes therefore offer unique possibility to explore fundamental properties of quasi-onedimensional systems. In this seminar we will focus on electric and transport properties. One of the most amazing characteristics of carbon nanotubes is that they can be metallic or semiconducting, depending on their structure. Unfortunately, the production of nanotubes lacks good control of exact structure of resulting nanotubes [5].

In this seminar, we will mostly focus on single wall carbon nanotubes. After brief presentation of carbon nanotubes synthesis and structure, the zone folding approximation for calculating electronic band structure will be discussed. Effect of bundling, defects and multiwall nanotubes will be also discussed. The second part of the seminar will present application of Landauer formalism on quasi-onedimensional transport in carbon nanotubes.

2 Synthesis and structure of carbon nanotubes

The mechanism of nanotube growth is not yet clear and is one the main challenges in the field of nanotubes synthesis [5]. We will therefore only mention the most important methods for production carbon nanotubes without explaining the mechanism of growth. All the main methods for production carbon nanotubes involve high temperatures. Condensation of hot gaseous carbon atoms generated by evaporation of solid carbon is the main process involved in arc discharge and laser vaporization method. Resulting nanotubes are tangled into bundles. Growth of SWNTs with these two methods is possible in the presence of a metal catalyst. The third method, chemical vapor deposition (CVD)



Figure 1: Carbon nanotube is a member of the graphitic family which includes also graphene and buckyballs. Graphene can be stacked into graphite, rolled into carbon nanotubes or wrapped up into buckyballs [1].

involves decomposition of gaseous compounds of carbon (CH_2 , C_2H_2 , C_2H_4 , C_6H_6 or CO). Catalysts for the deposition are metallic nanoparticles, which also serve as nucleation sites for initiation of nanotube growth. The CVD method has been developed for producing both MWNT and SWNT and has become the most important commercial method for SWNT production [5]. With CVD-based synthesis methods one can produce well-separated individual SWNTs.

The structure of carbon nanotubes is closely related to the structure of graphene, which is described as a Bravais lattice with a basis. On figure 2 the primitive vectors are shown: $\mathbf{a}_1 = (3/2a, \sqrt{3}/2a)$ and $\mathbf{a}_2 = (3/2a, -\sqrt{3}/2a)$, where *a* is the length of carbon-carbon bond. Basis vectors are $\mathbf{d}_1 = \mathbf{0}$ and $\mathbf{d}_2 = (0, a)$. The graphene sheet can be rolled into a cylinder in infinitely many ways. Rolling is described with the circumferential vector, denoted by \mathbf{C}_h (figure 2). As we shall see, the way of rolling is extremely important for the nanotube properties. Circumferential vector is expressed in terms of primitive vectors of graphene sheet: $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$. Nanotubes are classified into the three groups according to values of *n* and *m*:

- armchair tubes (n, n) C-C bonds are perpendicular to the tube axis
- zig-zag tubes (n, 0) C-C bonds are parallel to the tube axis
- chiral tubes $(n, m \neq n)$.

Examples for each of the classes are shown in figure 2. In this seminar, we will consider nanotubes as onedimensional (or quasi-onedimensional) objects. The primitive vector of onedimensional lattice is the shortest vector of the graphene lattice, perpendicular to \mathbf{C}_h . It is denoted by \mathbf{T} and expressed in terms of primitive vectors of graphene lattice: $T = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2$ (figure 2). Since the condition $\mathbf{C}_h \cdot \mathbf{T} = 0$ must be satisfied, t_1 and t_2 can be expressed in terms of m and n:

$$t_1 = \frac{2m+n}{N_R}, \qquad t_2 = -\frac{2n+m}{N_R},$$

where N_R is the greatest common divisor of (2m+n) and (2n+m). The number of carbon atoms in the primitive cell also depends on the integers n and m:

$$N_C = \frac{4(n^2 + nm + m^2)}{N_R}$$

Common synthesis methods result in mixtures of nanotubes with different chiralities, i.e. different pairs of indices n and m and also with major concentration of impurities. Therefore additional processing is necessary for obtaining pure samples of nanotubes with desired geometry and organization.



Figure 2: Left: graphene sheet is a honeycomb lattice. Primitive cell (shaded) contains two carbon atoms. Primitive vectors are $\mathbf{a_1}$ and $\mathbf{a_2}$. *a* is the length of C-C bond. $\mathbf{C_h}$ is a circumferential vector for a tube (2, 1) and \mathbf{T} is a primitive vector of onedimensional lattice for the same tube. Right: zig-zag tube (12,0), armchair tube (6,6) and chiral (6,4)tube [4].

3 Electronic properties of carbon nanotubes

Electronic band structure of graphene

Carbon has four valence orbitals: 2s, $2p_x$, $2p_y$ and $2p_z$. In graphene, planar 2s, $2p_x$ and $2p_y$ combine to form three hybridized σ orbitals. The p_z orbital does not couple with σ orbitals for symmetry reasons [4] and is called π orbital. On figure 3 the σ and π orbitals of each individual carbon atom in graphene are schematically presented. Since there are two carbon atoms in the primitive cell of graphene, eight energy bands arise from valence atom orbitals. The first Brillouin zone of graphene is presented in figure 3. Figure 4 presents calculated energy bands in M- Γ -K directions in the k space. The bonding (occupied)



Figure 3: Left: The carbon valence orbitals: inplanar σ and perpendicular π orbitals [6]. Right: reciprocal or lattice of graphene is real space Bravais lattice of graphene, rotated for $\pi/2$. The first Brillouin zone is shaded and the three important points are noted: center (Γ), corner (\mathbf{K}) and middle of the edge (\mathbf{M}) point.

 σ and antibonding (unoccupied) σ^* bands are separated by a large energy gap and are far away from the Fermi level. Bonding and antibonding π bands, on the other hand, do cross at the K point. Fermi surface is therefore reduced to the six K points at the corners of the first Brillouin cone. As a consequence, graphene is a zero-gap semiconductor or semimetal [4]. Near the Fermi energy π and π^* bands have linear dispersion relation. Electron and holes near Fermi surface usually have quadratic dispersion relation and behave as free particles with effective mass $m^* \neq m_e$. Linear dispersion is typical for massless Dirac fermions, i.e. particles with relativistic speed and no mass. However, while being in general an important



Figure 4: Left: Electron band structure of graphene from *ab-initio* calculations in the M- Γ -K direction in the k space [4]. Fermi energy is set to zero electron volts. The dotted line is the vacuum level and Φ represents the work function. The two π bands arise from carbon p_z orbitals and the six σ orbitals arise from s, p_x and p_y orbitals. π bands cross at the K point and have linear energy-momentum relation. Right: results of the tight binding method and *ab-initio* calculations [4]. Agreement is very good near the K point.

notion, it will not be discussed further in this seminar.

It is convenient to have an analytical expression for the dispersion relation and related eigenstates. For graphene, the tight binding method approximation gives good results near Fermi level. Since bonding and antibonding σ are too far away from Fermi level to play a role, we can focus on π bands. When accounting only for nearest neighbor interactions, we get:

$$E(\mathbf{k}) = \pm \gamma_0 \sqrt{3 + 2\cos(\mathbf{k}\mathbf{a}_1) + 2\cos(\mathbf{k}\mathbf{a}_2) + 2\cos(\mathbf{k}(\mathbf{a}_2 - \mathbf{a}_1))},$$
(1)

where γ_0 is the transfer integral between first neighbor p_z orbitals. Its value is around 3 eV [4]. Results of *ab initio* calculations are compared to results from the tight binding approximation in figure 4. Expansion of expression 1 in vicinity of the K point ($\kappa = \mathbf{k} - \mathbf{K}$) is:

$$E^{\pm}(\kappa) = \pm \hbar v_F |\kappa|.$$

Fermi velocity for electrons in graphene is $v_F = 1 \times 10^6 m/s$.

From graphene to nanotubes

For calculating electronic band structure in carbon nanotubes we will use the zone-folding approximation. The idea is to take the graphene electronic states and to account for the periodic boundary condition in the circumferential direction. The periodic boundary condition for a nanotube wavefunction ψ_{nt} is:

$$\psi_{nt}(\mathbf{r}) = \psi_{nt}(\mathbf{r} + \mathbf{C}_{\mathbf{h}}). \tag{2}$$

Since C_h is a Bravais lattice vector of graphene we can use the Bloch theorem¹ for the graphene wavefunction:

$$\psi_g(\mathbf{r} + \mathbf{C_h}) = e^{i\mathbf{k}\cdot\mathbf{C_h}}\psi_g(\mathbf{r}). \tag{3}$$

Combining equations 2 and 3, we see that the nanotube states are the same as the set of graphene states in directions in reciprocal space that satisfy the following condition:

$$\mathbf{k} \cdot \mathbf{C}_h = 2\pi q, \quad q \in \mathbb{Z}. \tag{4}$$

This condition does not affect values of \mathbf{k} in the direction parallel to the tube axis. Allowed states belong to lines in reciprocal space of graphene that are parallel to the tube axis and have distinct values of \mathbf{k}_{\perp} . See figures 5 and 6 for examples. The first Brillouin zone in onedimensional nanotube reciprocal space is a line segment with length $\frac{2\pi}{|\mathbf{T}|}$. From now on, we will denote the onedimensional reciprocal vector as k. For every allowed direction we get two energy bands. Number of all bands should be equal to

¹The eigenstates of electrons in a periodic potential can be chosen to have a form of a plane wave times function with the periodicity of the potential [7].



Figure 5: Nanotube (2, 0). Circumferential vector $\mathbf{C}_{\mathbf{h}}$ and vector \mathbf{T} in real space graphene lattice are shown on the left. The reciprocal graphene lattice is rotated for $\pi/2$. Allowed wave vectors lie along red lines. Onedimensional first Brillouin zone is a line segment $\left[-\frac{\pi}{|\mathbf{T}|}, \frac{\pi}{|\mathbf{T}|}\right]$. The K point of the graphene first Brillouin zone is not an allowed state for (2,0) nanotube.



Figure 6: Nanotube (2, 2). Allowed wave vectors lie along red lines. The K point is allowed for (2,2) nanotube.

the number of carbon atoms in a two dimensional unit cell $(\mathbf{T} \times \mathbf{C_h})$ of a tube. Usually, there is some degeneracy and the number of different energy bands is smaller. Resulting energy bands for an armchair (5,5) nanotube, zig-zag (9,0) and zig-zag (10,0) nanotube are presented on figure 7. The first two are zero gap semiconductors, since valence and conduction bands cross at $k = 2\pi/3a$ (armchair) and k = 0 (zig-zag (9,0)). At finite temperature they exhibit metallic conduction and usually they are referred to as metallic. The third nanotube, (10, 0) is semiconducting, since it has finite energy gap (1 eV). Nanotube is semiconducting if the allowed k values do not include the K point of graphene's first Brillouin zone. The K point is included in allowed states if $\mathbf{K} \cdot \mathbf{C_h} = 2\pi q$, where q is an integer. We choose, for example, the point K with $k_x = 0$ and $k_y = 2\pi/a \cdot 2/3\sqrt{3}$. Therefore:

$$\left(0, \frac{2\pi}{a} \frac{2}{3\sqrt{3}}\right) \cdot \left(n\mathbf{a_1} + m\mathbf{a_2}\right) = 2\pi q \tag{5}$$

$$\frac{2\pi}{3}(n-m) = 2\pi q.$$
 (6)

The condition 6 is satisfied for armchair nanotubes (n - m = 0), for the subset of zig-zag nanotubes with n = 3l and can be satisfied by chiral nanotubes as well. Now we have an explanation for the (non)metallic character of our examples in figure 7.

The energy gap, which appears in semiconducting nanotubes $(n - m = 3l \pm 1)$, can also be calculated



Figure 7: Energy bands for armchair (5,5), zig-zag (9,0) and zig-zag (10,0) tube, obtained by the zone folding approximation [4]. Γ is the center and X is the edge of the one-dimensional first Brillouin zone. Fermi level is located at zero energy. In first two cases, valence and conduction band cross and the nanotubes are metallic. The third nanotube is semiconducting, having the energy gap of 1 eV.

from dispersion relation in vicinity of the K point [4]:

$$\varepsilon_q^{\pm}(k) \approx \pm \frac{3a}{2} \gamma_0 \sqrt{\left(\frac{2\pi}{|\mathbf{C}_{\mathbf{h}}|}\right)^2 \left(q \pm \frac{1}{3}\right)^2 + k^2} \tag{7}$$

$$\Delta E_g = \varepsilon_{q=0}^+ (k=0) - \varepsilon_{q=0}^- (k=0) = \frac{2\pi a \gamma_0}{|\mathbf{C}_{\mathbf{h}}|} = \frac{2a \gamma_0}{d_t}.$$
(8)

The energy gap decreases as the inverse of the tube diameter d_t . In the limit of infinite diameter there is no gap as graphene is revealed.

A quantity that is closely related to the dispersion relation is the density of states. It represents the number of states available for a given energy interval. Under some assumptions it can be measured experimentally using scanning tunneling microscopy. This kinds of experiments confirmed that the energy gap in semiconducting nanotubes is proportional to $1/d_t$ [4].

Curvature effects

Carbon nanotubes are not just stripes of graphene but small cylinders. There are three important consequences of the finite curvature of nanotubes:

- C-C bonds perpendicular and parallel to the axis are slightly different and therefore the basis vectors **a**₁ and **a**₂ are not of equal length anymore;
- formation of an angle for the p_z orbitals located on bonds not strictly parallel to the axis yield differences in hopping terms (γ_0) between carbon atom and its three neighbors;
- the π and σ states can mix because the planar symmetry is broken.

The first two effects change condition for the Fermi point so that it is no longer the K point of graphene Brillouin zone. It turns out that only armchair tubes keep their metallic behavior. In zigzag and chiral metallic nanotubes the Fermi point is no longer included in the allowed states and a small bandgap opens at the Fermi level. This band gap is called *secondary band gap* and it scales as $1/d_t^2$ (both theoretically predicted and experimentally observed) [4]. The secondary band gap is usually so small for zigzag nanotubes that all n - m = 3l (l=0,1,2,...) nanotubes can be considered as metallic at room temperature. For large diameter tubes the simple band folding approximation continues to be valid as well.

Rehybridization that appears among σ and π states in small nanotubes $(d_t < 1nm)$ alters the electronic properties significantly. The zone folding approximation may fail completely. As an example we consider (6,0) nanotube with diameter $d_t = 0.5nm$. This tube is predicted to be a semimetal with zero bandgap in the band-folding scheme. Hybridization makes it a true metal since band overlap occurs.

Bundles, multiwall tubes and defects

Single wall carbon nanotubes, grown by standard methods mentioned in the chapter 2, always occur in bundles of 10-100 nanotubes [4]. Nanotubes in a single rope have approximately the same diameter but different chiralities. Electronic properties of course change with bundling, even for perfectly ordered nanotubes with uniform chirality. For example, in a bundle of hexagonally ordered (10,10) nanotubes a pseudogap of a 0.1 eV occurs [4]. A pseudogap is an energy interval (usually near Fermi level) with very low density of states, but not precisely zero as for the gap. In semiconducting (8,4) nanotube, on the other hand, bundling results in a decrease of the energy gap [8].

Multiwall carbon nanotubes consist of nested single-wall nanotubes. Van der Waals interaction between layers may have important effects on the electronic properties of constituent isolated nanotubes. Interwall coupling opens a pseudogap, as in the case of bundling. Appearance and size of a pseudogap depend on the mutual orientation of the constituent tubes [4], see figures 8 and 9.



Figure 8: Band structures of the same double-wall nanotube for different relative orientations [9]. The Fermi level is shown by the dashed line. The nanotube consists of (5,5) and (10, 10) SWNT. (a) Band structure without interaction. (b)The most symmetric configuration: zero gap. (c) Less symmetric configuration results in four avoided crossings of bands.



Figure 9: Density of states near Fermi level for double-wall carbon nanotube (5,5)@(10,10); orientation the same as in figure 8(c). Four pseudogaps are easily deduced [9].

Until now we were discussing perfect, infinite nanotubes. In reality, nanotubes have finite length and defects such as pentagons, heptagons, vacancies, adatoms and substitution impurities. All these imperfections at least locally modify electronic properties of the host tube. Topological changes at the end of the nanotube, where the nanotube closes itself, modify electronic properties fairly locally. They initiate sharp resonances in the density of states near Fermi energy. There is also another consequence of the finite length of the nanotube—electrons can only have discrete values of kinetic energy. The energy spacing in a particle-in-a-box model is $h^2/2mL^2$, where L is a length of a box. If the energy spacing is much higher than the thermal energy, the system acts as an insulator, since all of the bands are completely occupied or completely empty. According to this argument, a 100 nm long metallic nanotube becomes an insulator well under 2 K and a 30 nm long nanotube becomes an insulator well under 22 K. The eigenstates for a particle in a box are the standing waves. The standing waves were indeed experimentally observed, for example, in an armchair nanotube with diameter $d_t=1.5$ nm and length L=30 nm [10]. STM tunneling conductance (dI/dV) measurements at low energies (order 0.1 eV) are proportional to electron density [10], in contrast to higher energy measurements, which are proportional to density of states, as mentioned earlier (page 7). Wavelengths of standing waves were near the theoretically predicted Fermi wavelength. At different voltages standing waves with different wavelengths were observed (figure 10).



Figure 10: Spectroscopy and topography line scans along the armchair nanotube [10]. A and B: Electron wavefunctions at four different energies have wavelengths from 0.66 nm to 0.76 nm. C: Topographic height profile reveals lattice constant 0.25 nm, clearly different from period $\lambda/2 = 0.4$ of standing waves.

4 Electrical transport in single-wall carbon nanotubes

Electrical transport in macroscopic conductor

Electrical conduction in bulk materials is described by the Ohm law $\mathbf{j} = \sigma \mathbf{E}$ or I = U/R, where resistance R depends on the size of the conductor and size independent conductivity σ . In order to predict the conductivity, we need to develop the microscopic theory of conduction. The simplest way is to consider the conducting electrons as free and independent particles. The average current density is proportional to the mean velocity. If there is no external field, the mean velocity is zero. When we turn on the electrical field, each electron starts to accelerate until it scatters of a phonon or impurity. Mean velocity of electrons and conductivity are therefore proportional to the average time between two 'collisions' of each individual electron (τ) [7]:

$$\langle \mathbf{j} \rangle = -ne_0 \langle \mathbf{v} \rangle; \qquad \langle \mathbf{v} \rangle = -e_0 \mathbf{E} \tau / m$$

$$\sigma = ne_0^2 \tau / m.$$

Without the scattering the conductivity would be infinite. An important physical quantity, connected with scattering, is also the mean free path: $L_0 = \langle \mathbf{v} \rangle \tau$.

A better theory is a semiclassical approximation, which deals with electrons in a periodic potential in a crystal — so called Bloch electrons. The electrons are localized on a scale that is much smaller than the the variation of electric field. In this approximation, the conductivity depends on the dispersion relation of electronic states and on relaxation time. The famous Boltzmann equation accounts also for the density of states dependence of relaxation time [7].

The above discussion is of course valid for normal conductors only. In superconductors, a fraction of electrons propagates without scattering, which leads to perfect conductivity.

The Landauer approach for describing quasi-onedimensional transport

In the Landauer approach, the electrical current through a conductor is expressed in terms of the probability that an electron can pass through it (transmission probability T).

Consider a quasi-onedimensional conductor (a SWNT in our case) stretched between two large contact pads (figure 11). Applying Ohm law in one dimension, we get $I = \sigma/LU$, where σ is length independent. When reducing the length of the conductor, the conductance grows towards infinity. Measurements show, however, that conductance in fact approaches finite limiting value.



Figure 11: Quasi-onedimensional conductor is stretched between two large contact pads. We investigate the current flowing through it after the voltage is applied. Note that the contacts are three dimensional and the conductor is quasi-onedimensional.

It turns out that the current through the conductor is finite even for a ballistic conductor, i.e. when there is no scattering in the conductor and the transmission probability equals one. Conductor is in ballistic regime, when its length is much shorter than electronic mean free path. Resistance in a quasionedimensional conductor is a consequence of the rapid change of dimensionality on the contacts and is called *contact resistance*. In order to clarify the origin of the contact resistance, we will derive the conductivity of ballistic (and later on also non-ballistic) quasi-1D conductor, following the reference [11].

States in a quasi-onedimensional conductor belong to different subbands and each of these subbands has its own dispersion relation E(n, k). Total current is a sum of currents carried by each subband. Therefore we can first calculate the contribution of one subband.

A uniform electron gas with n electrons per unit length moving with velocity v carries a current I = nev $(e = -e_0)$. Electron gas in our conductor is not uniform; states with positive k originate in the left contact and are occupied according to the Fermi-Dirac distribution $f^+(E(k))$ and states with negative k originate in the right contact and are occupied according to Fermi-Dirac distribution $f^-(E(k))$. For simplicity, we will only calculate for the zero temperature case. Fermi levels in the two contacts are not the same because of the applied voltage. Total current is:

$$I = I^{+} - I^{-} = \frac{e}{L} \sum_{k>0} v(k) f^{+}(E) + \frac{e}{L} \sum_{k<0} v(k) f^{-}(E).$$
(9)

The group velocity of electrons in the particular energy band is proportional to the derivative of energy with respect to k: $v = 1/\hbar \cdot \partial E/\partial k$ [7]. Velocity is therefore an odd function of the wave vector k and we get:

$$I = \frac{e}{L} \sum_{k>0} \frac{1}{\hbar} \frac{\partial E}{\partial k} (f^{+}(E) - f^{-}(E)).$$
 (10)

The sum over k can be converted into an integral using the prescription

$$\sum_k \rightarrow 2 ({\rm spin \ degenaracy}) \times \frac{L}{2\pi} \int dk.$$

We obtain

$$I = \frac{e}{\pi\hbar} \int_0^\infty (f^+(E) - f^-(E)) \frac{\partial E}{\partial k} dk = \frac{2e}{\hbar} \int_{E_{min}}^{E_{max}} (f^+(E) - f^-(E)) dE.$$
(11)

At zero temperature, electrons fill all the states from zero to Fermi energy. The difference $f^+ - f^-$ is therefore a rectangular function with nonzero value from μ_2 to μ_1 (figure 12 left). We can now easily



Figure 12: Left: Fermi levels in the left (1) and right (2) contact are μ_1 and μ_2 , respectively. At zero temperature Fermi distribution is a step function and the difference $f^+(E) - f^-(E)$ is a rectangular function. Right: Energy levels in a conductor. Free-electron like dispersion is shown only for simplicity.

evaluate the integral in equation 11:

$$I = \frac{2e}{h}(\mu_1 - \mu_2) = \frac{2e^2}{h}\frac{\mu_1 - \mu_2}{e} = \frac{2e^2}{h}U.$$
 (12)

The conductivity per subband is equal to $G_0 = \frac{2e^2}{h}$. Now we calculate the current arising from all contributing subbands. Subbands with lowest energies higher than μ_1 do not contribute to the current. Defining the number of subbands with cutoff energy lower than E, M(E), the total current is calculated by:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} (f^+(E) - f^-(E))M(E)dE = \frac{2e}{h} \int_{\mu_2}^{\mu_1} M(E)dE$$

Assuming that M(E) is constant over the energy range $\mu_2 < E < \mu_1$, each of the M bands contributes a quantum of conductivity G_0 (see figure 12 right). Contact resistance is therefore

$$R_c = \frac{1}{M \cdot G_0} = \frac{12.9k\Omega}{M}.$$

For non-ballistic conductor transmittance T is less than one. We can use a classical model that predicts

$$T = \frac{L_0}{L_0 + L},$$

where L_0 is mean free path of electrons and L is length of conductor. In limits $L_0 \gg L$ we get ballistic conductance and for $L \ll L_0$, and assuming a wide conductor, we get Ohm law. Proof of this model can be found in reference [11].

Total resistance can be viewed as sum of the contact and tube part [12]:

$$R = R_c + R_t = \frac{1}{M \cdot G_0} + \frac{L}{L_0} \frac{1}{M \cdot G_0}.$$

To apply the Landauer theory to carbon nanotubes, we need to recall the knowledge about electronic band structure. Metallic armchair nanotubes present two conduction channels at the Fermi energy leading to conductance $2G_0$ (figure 13)—resistance 6 k Ω . They often approach this value even at room temperature. For semiconducting nanotubes conductance is usually smaller. To explain the lower conductance, we need to consider the additional contacts or tube contribution to resistance. Different sources of resistance add incoherently at room temperature. At lower temperatures quantum effects become important.



Figure 13: Band structures and conductances for metallic (5,5) and semiconducting (10,0) carbon nanotube [6]. The latter is given simply by number of bands at energy E and for k > 0.

It is interesting to make a comparison between conduction of carbon nanotubes and conduction of a copper nanowire of the same size. As typical dimensions, the diameter $d_t=1$ nm and length L=100 nm can be taken. Mean free path of electrons in bulk copper at room temperature is 40 nm, which is therefore the upper limit for the mean free path of electrons in the copper nanowire [13]. Conduction in a 100 nm long copper nanowire is in the quasi-ballistic regime, since the mean free path of electrons is smaller, but comparable in size with the length of the device. Transmission coefficient is less than one: $T = L_0/L_0 + L \approx 0.29$. The number of conducting channels depends on the diameter of the nanowire and equals 5 for the diameter $d_t=1$ nm [14]. The resistance is:

$$R = R_c + R_w = \frac{1}{M \cdot G_0} + \frac{L}{L_0} \frac{1}{M \cdot G_0} = (1 + 2.5) \frac{1}{M \cdot G_0} = 9 \text{ k}\Omega.$$

For the chosen size of the copper wire the resistance is comparable to the resistance of the carbon nanotube. But since both M and T are size dependent we can get a larger difference. For example, for a longer wire — L=1 μ m with the same diameter, the resistance is 65 k Ω . The real value of resistivity can be larger, since we took the upper limit of the mean free path of electrons. However, in ballistic regime of conduction, higher values of current densities can be carried than in non-ballistic regime. The first is available for nanotubes in wider range of lengths than for copper nanowires.

Classical (incoherent) transport

If we neglect coherence effects, the total resistance of a nanotube is simply a sum of contact resistance and tube resistance as mentioned above. For semiconducting nanotubes contact resistance may be larger as $1/MG_0$ due to the Schottky barrier. The height of the barrier depends on the work function of a metal and on the energy gap of a nanotube. Good contact for p conducting tubes is achieved with Pd contact and for n type tube with Al contact. Since the energy gap depends on radius of a tube, this applies to the barrier as well. Pd contact, for example, makes a good contact with nanotubes with radius greater than 1.5 nm [12].

Nanotube resistance, denoted R_t , arises from scattering phenomena. Electron scattering on the defects is temperature independent, while scattering on the phonons is not. For a bulk material, scattering on defects only becomes important at low temperatures, in absence of phonon scattering [7]. Defects in nanotubes, on the other hand, may have significant effect even at room temperature. Typical mean free path of electrons at low temperatures for metal nanotubes is many microns and of the order of a micron for semiconducting tubes. Origins of disorder [12] are:

- localized defects: vacancies, substitutions, pentagon-heptagon defects, heterojunctions between nanotubes of different chiralities;
- electrostatic potential fluctuations, created by charges in substrate and by molecules, adsorbed on the nanotube;
- mechanical deformations, such as local strains and twists, which affect the local bandgap and as kicks that act as conductance barriers.

Quantum effects

At low temperatures there were many interesting effects observed, which indicate the importance of electron—electron interaction. Coulomb interactions cause electron—electron scattering near Fermi level. In three- and two-dimensional electronic systems scattering is strongly suppressed by restrictions of energy and momentum conservation combined with Pauli's exclusion principle [15]. The theory describing weakly interacting electrons (fermions) is called Fermi liquid theory. In this theory, the system is described with an independent quasiparticle approximation (instead of independent electron approximation for noninteracting electrons) [7]. The charge and spin of the quasiparticles are $-e_0$ and 1/2, respectively. Onedimensional system of interacting fermions behaves differently, since electron—electron scattering is less suppressed. The name for this kind of system is Luttinger liquid. Spin and charge excitations are described as bosonic modes, are separable and propagate at different velocities [12]. There are power-law dependencies expected in transport. Experiments measuring the dependence of conductance on temperature and gate voltage in carbon nanotubes confirmed 'luttinger-like' behavior [12].

5 Conclusion

The band-folding approximation gives a good first information about electron band structure of carbon nanotubes. We find that metallic/semiconducting character of single-wall nanotubes crucially depends on the chirality. Including curvature effects we find that only the armchair nanotubes are always metallic. Bundling of single-wall armchair nanotubes and incorporating them into multiwall nanotubes effects opening of pseudogaps.

The conductivity of metallic single-wall carbon nanotubes is ballistic even at room temperature. We derived their conductivity using the Landauer approach for quasi-onedimensional transport. For nanotubes in non-ballistic regime, possible origins of defects were given. At the end, quantum effects were briefly mentioned.

High conductivity of metallic nanotubes makes them appealing as building blocks of future molecular electronics circuits. They are also likely to play a key role in future electronics applications, including quantum computing [3]. Controlled production of carbon nanotubes with a well-defined atomic structure —chirality, still remains a problem, holding back the (large-scale) realization of many suggested applications [3].

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