Electrical Characterisation of Free Standing Multiwalled Carbon Nanotubes

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For my parents
Abstract

Two terminal electrical measurements of freestanding multiwalled carbon nanotubes employing tunnelling contacts have been made. Previous electrical characterisation on both single and multiwalled carbon nanotubes have revealed a zero bias anomaly, in which the current is characterised by a power law ($I \propto V^{\alpha}$). In the case of single wall nanotubes this behaviour has been explained within Luttinger liquid theory, the strong repulsive electron-electron interactions found in one dimension causing Fermi liquid theory to break down. The origin of the power law in the characteristics of multiwalled nanotubes is less clear and is the subject of considerable debate. In part, the debate is fuelled by the very similar predictions of the various theories, particularly those of Luttinger liquid and single junction Coulomb blockade theory.

The measurements presented in this thesis employ a unique combination of a freestanding geometry with high resistance tunnelling contacts, which are necessary to probe electron-electron interactions. The results are quantitatively very different to all previous reports and are explained using the environmental quantum fluctuations found in single junction Coulomb blockade.

The size of the quantum fluctuations is strongly influenced by the high frequency impedance of the nanotube. The freestanding geometry causes reflections within the nanotube, resulting in an impedance-frequency characteristic significantly different to that expected for conventional on-substrate geometries. It is proposed that this is the cause of the large quantitative difference between the results gained from the freestanding geometry and the on-substrate geometry.

The exponent, $\alpha$ which characterises the power law ($I \propto V^{\alpha}$) is typically around 0.3 in the conventional on-substrate geometries (both theoretically and experimentally). The original results presented in this thesis show $\alpha \sim 3.5$ and the exponent shows considerable variation. The non-conventional freestanding geometry, splits for the first time, the predicted exponent from Luttinger liquid and environmental quantum fluctuations theories as they are applied to multiwalled carbon nanotubes. The later interpretation is favoured not only because of the quantitative agreement with the exponent, $\alpha$ but unlike Luttinger liquid theory it is also in agreement with other experimental observations, such as offset ohmic behaviour. The agreement is such
that these results could be the best demonstration of environmental quantum fluctuations in a single junction Coulomb blockade.

The power law in MWNTs appears to have several manifestations. Uniting them all in a single explanation could well be impossible. So, while this work may not end the debate on the origin of the power law in MWNTs it certainly will make a significant contribution.
Acknowledgements

The experimental work in this thesis would not have been possible without the close collaboration and support of David Cox and Roy Forrest. Outside of the laboratory, I would like to thank my supervisors; David Carey for the many helpful discussions and Ravi Silva for his guidance, patience and trust throughout. I would also like to thank the rest of the research group for their support and making it a great place to study.

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Glossary of Terms

AFM  Atomic force microscope
CB   Coulomb blockade
CNT  Carbon nanotube
CVD  Chemical vapour deposition
DOS  Density of states
e-beam  Electron beam
EFM  Electrostatic force microscope
EG   Egger- Gogolin theory
EM   Electromagnetic
EQF  Environmental quantum fluctuations
FL   Fermi liquid
IC   Integrated Circuit
KFM  Kelvin force microscopy
LC   Inductance and Capacitance
LCR  Inductance, capacitance and resistance
LL   Luttinger Liquid
MO   Molecular orbital
MWNT Multiwalled carbon nanotube
RF   Radio frequency
<table>
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<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SPM</td>
<td>Scanning probe microscopy, collective term for techniques such as AFM, STM etc.</td>
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<td>STM</td>
<td>Scanning tunnelling microscope</td>
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<tr>
<td>SWNT</td>
<td>Single wall carbon nanotube, sometimes prefixed with m- or s- denoting metallic and semiconducting respectively</td>
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<tr>
<td>TDOS</td>
<td>Tunnelling density of states</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>WL</td>
<td>Weak localisation</td>
</tr>
<tr>
<td>ZBA</td>
<td>Zero bias anomaly</td>
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1 Introduction

Since their discovery by Iijima, (1991) carbon nanotubes have had a big impact, fuelling much scientific advancement. Hand in hand with the science has gone a broad spectrum of potential industrial applications, from the enhancement of existing products to the development of entirely new ones. Iijima’s initial discovery was of multiwalled carbon nanotubes (MWNTs), that consist of many concentric graphene tubes, but a nanotube can be formed of just a single graphene sheet.

Single walled carbon nanotubes (SWNT) are far simpler structures, but their multiwalled counterparts (MWNTs) are much more amenable experimentally. It is not the case that one form is superior to another; rather, it depends on the balance of properties required for a particular application. It is often the case in scientific applications that SWNTs are favoured over MWNTs. The reasons for this lie in the theoretical attraction of SWNTs. They are smaller, simpler systems whose basic properties are well established and can be simulated more easily using ab initio calculations, as well as theoretical works. MWNTs are complicated; they introduce many unknowns that essentially stem from how the walls interact with each other, and unlike SWNTs whose entire structure is on display, the internal structure of MWNTs is hidden from view.

Our understanding of electrical conduction in MWNTs is therefore an area where not only is there scope for progress, but the advancement of understanding would prove to be useful both for science and industry. Such motivations make it an active field of research, with considerable progress having been made in recent years. However, despite recent progress, aspects of conduction in MWNTs such as the phenomenon of the zero bias anomaly (ZBA), or rather the power law behaviour ($I \propto V^{\alpha}$) elude a definitive explanation.
The project started with a broad aim: To investigate conduction in MWNTs. The aims lead to the development of an unconventional experimental set-up within a scanning electron microscope (SEM). The unconventional experimental set-up soon yielded original results enabling the aims to be focused.

The central objective of the project became the explanation of our own original results. Qualitatively similar results had been reported before, but these could never be explained definitively. As several theories, all predicting similar behaviour could not be separated by the experimental results gained from conventional set-ups.

The striking quantitative difference in our results, from those of conventional experimental set-ups meant there was a good chance the interpretation of our data would allow the predictions of the different theories to be split (and it did). Therefore, the interpretation of our data not only gives an insight into phenomena as observed in our experimental set-up, but also the phenomena as it is observed elsewhere around the world in MWNTs.

1.1 Thesis Layout

Chapter 2 briefly introduces carbon nanotubes, how they are made and some examples of their present and future applications.

Chapter 3 aims to provide all the background information necessary to for evaluating the results and to explain them. The basic theoretical concepts are introduced as they become necessary and usually accompanied with an example, although the intertwining of the literature review with the essential theoretical concepts does make this chapter the largest.

Given the importance and various classes of carbon nanotubes, conduction in nanotubes is now a large field. Chapter 3 is not intended to be a comprehensive literature review but a taster to the key papers and concepts out there. From section 3.9 onwards all studies feature comparable measurements to those in chapter 4. Up to section 3.9, much of the featured work was chosen because it provided a suitable example of concept or principle, and one of many studies could have been chosen although occasionally some of the work highlighted is unparalleled. The theoretical work featured is very much limited to those which relate directly to experimental studies.
The experimental set-up is described in Chapter 4 before the results are presented, together with preliminary analysis. The nature of the experimental set-up means that the power law behaviour requires a careful and detailed analysis, if the conclusions drawn with regard to the explanation are to be sound. This detailed analysis and the comparison with theory is contained within Chapter 5. Following this, conclusions and directions for future research is presented in chapter 6.
2 Carbon Nanotubes

This chapter introduces carbon nanotubes, some of their basic properties, and how they are made. Some details as to the potential applications of carbon nanotubes are presented.

2.1 What is a Carbon Nanotube?

Graphite is a material formed of layers; it has a two-dimensional hexagonal shaped lattice consisting of covalently bonded carbon, whose layers are held together by relatively weak Van der Waal forces. When a single sheet of graphite, better known as graphene, is small enough it becomes energetically favourable for it to roll up (Figure 2.1), forming a single walled nanotube (SWNT). The small enough criteria means SWNTs typically have diameters around 1 to 3 nm. The length, however, can vary enormously, commonly produced with lengths of a few to tens of microns, they can also be millimetres long, giving them an incredibly high aspect ratio. The cap of each of these nanotubes is made up of the normal graphitic hexagon shapes, with ‘pentagon defects’ to accommodate the ‘bowing’ or deformation of the structure.
Figure 2.1: Reproduced from Dresselhaus et al (1995). Three possible ways to roll a graphene sheet forming a SWNT. a) Arm Chair tube, b) Zig-Zag and c) a chiral tube.

Figure 2.1 illustrates just three of many ways in which a graphene sheet can be seamlessly rolled. The seamless rolling which leaves no dangling bonds is just one of the factors that makes carbon nanotubes chemically inert, a property that makes them experimentally practical. When rolling the graphene sheet there are two limiting cases, the armchair tube (Figure 2.1a) configuration where the sides of the hexagon lie perpendicular to the tube axis, and the zigzag tube (Figure 2.1b), where the sides of the hexagon lie parallel to the tube axis. All other tubes are chiral, the chirality defined by a wrapping vector \((n,m)\). The limiting cases above are \((p,p)\) or \((2p,-p)\) for an armchair tube and \((p,0)\) for zigzag tubes.

As will be shown later in section 3.1, the chirality has a big impact on the electronic structure, determining if the nanotube is a metal or a semiconductor and the magnitude of band gap. Saito et al (1992) calculated that assuming all \((n,m)\)
combinations are equally likely two thirds of tubes should be semiconducting, with the remaining third being metallic.

In much the same way that graphite is formed of layers of graphene, multiwalled nanotubes, (MWNTs) Figure 2.2, are single walled nanotubes arranged like Russian dolls, each tube completely enclosed within another, with no chemical, (i.e. covalent or ionic) bonding between them. As will be shown later each tube, or, rather shell, retains its own character. MWNTs are therefore made up of semiconducting and metallic shells.

![Figure 2.2: Diagram of a MWNT formed of four armchair tubes.](image)

Although Figure 2.2 shows a MWNT consisting of 4 shells, they typically have a few more, ranging up to around 25, giving them diameters of anything between 8 - 25 nm.
The typical lengths are also similar to SWNTs, microns to tens of microns. There are other types, or sub-sets of MWNTs, e.g. double and triple walled nanotubes. In addition, there can be a grey area (in semantic terms) between MWNTs and tubular carbon fibres, where the graphene plane is not parallel to the tube axis. The material presented in this thesis almost exclusively concerns only high quality carbon nanotubes where the graphene planes are parallel to the tube axis.

2.2 Synthesis

As with many semiconductors and their related materials, the techniques by which nanotubes are synthesised impact upon the material’s properties. Carbon nanotubes are no exception. They are typically produced in one of three ways:

- Chemical vapour deposition (CVD) or PECVD for plasma enhanced CVD,
- Arc discharge, and,
- Laser ablation.

They all involve heating of a carbon containing gas or vapour to very high temperature and most also use a catalyst material such as nickel and cobalt. The difference between each method lies in how these conditions are produced.

CVD tubes are produced by dispersing the catalyst particles on a substrate. This is then put into a furnace and heated to (~700°C), and the gas (e.g. acetylene or methane) is flowed over the surface. This method produces most nanotubes in the least time, but often gives lower quality MWNTs, although under the right conditions it is possible to grow SWNTs of a high quality.

The arc discharge process uses a catalyst mixed with carbon powder and pressed into a rod to provide the material. The rod is then used as one electrode of a carbon arc. Inside the arc, extremely high temperatures are reached (~3000 °C), creating a carbon vapour. This method produces tubes, with a fairly high degree of structural perfection in reasonable quantities. Without using a catalyst, MWNTs are produced. With the right choice of catalyst, it is also possible to produce SWNTs in this manner.

The laser ablation process hits a graphite target (with or without catalyst loading) with a high energy laser. Once again this produces the necessary conditions for nanotube formation, namely a tiny plume of carbon vapour and catalyst at high temperatures. In
order to keep the plume of gas at these high temperatures where the nanotubes form the whole process takes place in a furnace. A felt of high quality SWNTs is then deposited on the furnace wall.

2.3 Applications of Carbon Nanotubes

Carbon nanotubes have found many scientific applications, enabling previously impossible or impractical experiments. One recent example is the filling of SWNTs with linear polyyne molecules (Nishide et al 2006), Figure 2.3a. Linear polyyne molecules are normally very unstable, previously detected in space they are not normally found under terrestrial conditions. However, when encapsulated in SWNTs they are stable in a dry ambient at room temperature.

The potential industrial applications for carbon nanotubes are innumerable, some much closer to fruition than others. The applications span a wide range, in their potential impact and level of technological sophistication. At the less sophisticated end, carbon nanotubes have been added to composite materials used in products available today. Babolat make a tennis racquet with carbon nanotubes, resulting in a racquet five times stiffer than its carbon fibre counterparts. Kindred and Collins (2005), report on the use of MWNTs in O-rings for use in connections of car fuel lines. The high aspect ratio and electrical conductivity of MWNTs means that only a small concentration makes the O-ring electrically conductive and the base material’s desirable properties are better retained. This the quality of the seal is improved and the permeation of petrol through the material is reduced compared to the carbon black impregnated alternative.

In a more sophisticated use of the bulk properties, Zhang et al (2004) shows how CVD grown MWNT forests can be spun into twisted multi-ply yarns, Figure 2.3b. These fine, strong, tough yarns have potential applications as conducting fibres in fabrics, a technology which has end uses such as RF/microwave absorption, heating and wearable electronics. In a similar technique, Zhang et al (2005) fabricates transparent, conducting and flexible sheets, potently useful as transparent and flexible electrodes for displays, incandescent lighting/heating and whole range of other niche applications.
Possibly the most technologically complex application is for carbon nanotubes as a replacement of today's Si based technology. The scaling of Si has been relentless over the last 50 years and is set to continue for a little while yet. While the miniaturisation of transistors has consistently presented challenges, many of the upcoming problems are fundamental in nature. Taking control of the number and location of dopant atoms is an example. In the expected 25 nm technology node (~2009), the channel is predicted to contain 5 million atoms, and just 35 of those are dopant atoms (Kasper and Paul 2005), fast approaching the statistical limit.

One of the many potential advantages offered by carbon nanotube circuits is that they do not require dopants. In fact a five stage CMOS-type ring oscillator has been fabricated on one 18 μm long SWNT without dopants by Chen et al (2006), Figure 2.3c. Other advantages such as the ballistic/quasi ballistic transport mean nanotubes have a lot to offer. The performance of current devices suggests that carbon nanotube transistors could be operating at 900 GHz, Lin et al (2005). It is therefore the potential
speed carbon nanotubes offer, rather than their size which make carbon nanotubes so attractive.

Devices are not the only application of carbon nanotubes in microelectronics. Due to their strong covalently bonded structure, it has been reported that carbon nanotubes can withstand current densities up to between $10^8$ - $10^{10}$ A/cm$^2$. Whereas, electromigration limits copper to around $10^6$ A/cm$^2$. This combined with their dimensions makes them candidates for vias, in bunches or a single MWNT (e.g. Kreupl et al 2004 for a review) and perhaps in the longer term interconnects.

Despite the fundamental limits today’s Si-based technology is approaching, it is an unknown if an alternative could be mustered. Even more unpredictable is if any disruptive technology could prove more a reliable, superior in performance and a cheaper alternative. Promising raw material and a few high performance transistors do not add to an IC revolution by themselves. However, the carbon nanotube field is moving beyond an assessment of their performance potential and it is now starting to work though many of the challenges which need to be overcome before billions of the ‘right’ type of nanotube are in the ‘right’ place and connected together to form an all carbon nanotube integrated circuit.

- It has been shown by Terrones et al (2002) SWNTs can be made to join under electron bombardment and the resulting T or X junctions are stable.

- Aligned SWNTs are being grown along predefined paths using electric fields (Ural et al 2002) or guided by the atomic alignment on the surface of the substrate (Ago et al 2005), a technique which is likely to have a chirality preference. Alternatively, nanotubes can be grown separately and located in predefined positions with chemical markers, e.g. Rao et al (2003).

- With the development of techniques by Bachilo et al (2002) to map the relative quantity of specific chiral indices $(n,m)$ present within a sample, it has been noted by Bachilo et al (2003) how some growth techniques can produce a very narrow distribution of chiral angles. The Avouris group at IBM, following the alternative approach of chiral selection are about to report on the selective removal of nanotubes from a sample such that only one specific $(n,m)$ chirality of tube remains (Avouris et al 2006).
3 Background

3.1 Electronic Structure

The electronic band structure of carbon nanotubes will be defined starting from molecular orbital (MO) theory. Electron orbitals are often described by the shape created by plotting the region of space where there is a 90% chance of finding an electron. For each orbital or shell (named s, p, d, f) several shapes or configurations of shapes are observed. The s orbital corresponds to a spherical shape around the nucleus, while p orbitals consist of three orthogonal pairs of dumbbells. The shape of higher orbitals can produce increasingly complicated pictures.

Molecular orbital theory describes the electron orbitals as atoms are brought together to form molecules. The simplest example is that of two s orbitals being brought together to form σ (σ*), bonding (anti-bonding) molecular orbitals, shown in Figure 3.1a. As p orbitals combine, they form π and π* MOs. If more electrons are in bonding orbitals than anti-bonding orbitals then there is a net reduction in the total potential energy of the orbiting electrons (relative to the case of the isolated atoms), Figure 3.1b, hence it is energetically favourable for the atoms to bond.

In the case of graphene, two of the three ‘dumbbell’ shaped p orbitals, say in the x-y plane hybridise with one of the spherically shaped s orbitals to form the three sp² orbitals (still in the x-y plane), while the p orbital in the z-direction is left unaltered (Figure 3.1c). The equivalent MO energy diagram for graphene would place the sp² bonding orbitals far below the Fermi level and the π and π* orbitals at the Fermi level. It is these orbitals at the Fermi level, which delocalise over the whole lattice, which mix to form the conduction and valance bands that touch at the Fermi level. The touching bands classify graphene as a semi-metal. For bulk graphite p orbitals between the layers can hybridise weakly, although it is not considered a chemical
bond like the \( sp^2 \) bonds and conduction normal to the \( sp^2 \) bond plane (c-axis) is dominated by defects rather than \( p \) orbital overlap.

Figure 3.1: Molecular orbital theory. (a) Orbital shapes: as two s-atomic orbitals come together to form a new molecular orbital. (b) The energy diagram corresponding to (a). (c) The hybridised \( sp^2 \) bonds and the remaining \( p \) orbital of graphite.
Many of the interesting electronic properties exhibited by nanotubes are a direct consequence of the E-\( k \) (energy - propagation constant or momentum) dispersion relation for graphene, Figure 3.2a. The E-\( k \) dispersion for conventional semiconductors with a 3D lattice would require a 4D graph \((k_x, k_y, k_z, E)\), so the E-\( k \) relationship is plotted moving from various points (high symmetry points) within the lattice to others i.e. \( k_x, k_y, k_z \rightarrow k'_x, k'_y, k'_z \). The resulting 2D plot would show energy vs distance (in reciprocal space) along the vector \( k_{x,y,z} \rightarrow k_{x,y,z}' \). The sequential path formed by the vectors between these points is termed the Brillouin zone.

The Brillouin zone in graphene is made up of four points; \( K \rightarrow \Gamma \rightarrow M \rightarrow K' \)

- \( \Gamma \) is the maximum / minimum point shown as the centre in Figure 3.2a, (0,0),
- The points at which the conduction and valance band touch are the \( K \) and \( K' \) points of which there are two points per unit cell / Brillouin zone,
- \( M \) lies equidistant between the \( K' \) and \( K \) points.

The intersection of the Fermi level with this 4D E-\( k \) relationship for conventional semiconductors (i.e. fixing \( E = E_F \)) produces a 3D graph \((k_x,k_y,k_z)\) surface referred to as the Fermi surface. With graphite’s 2D lattice, the E-\( k \) dispersion becomes a sheet on a 3D graph, the shape often referred to as a light cone. The consequence is the Fermi surface becoming a Fermi line. This Fermi line at low energies forms a circle, tending to a point as \( E \) tends to the intrinsic Fermi level, where the bands touch. The natural progression continues to a Fermi point in the 1D sub-bands of a nanotube.

Figure 3.2a was created based on the tight binding calculations of Wallace (1947), considering only one plane of graphite, infinite in both directions. Calculating the one dimensional dispersion relation for a SWNT only requires a minor modification to this model. First \( k_x \) and \( k_y \) are re-defined as the two directions on a nanotube; \( k_{\text{axis}} \) and \( k_{\text{circumference}} \). Then the periodic boundary condition is imposed that, only \( k_{\text{circumference}} \) values corresponding to an integer number of wavelengths (of the electron wave function) around the circumference are allowed. Non-integer multiples of the wavelength result in destructive interference of the electron wave function. Hence, the probability of finding an electron is zero where \( k_{\text{circumference}} \) does not correspond to \( 1/n\lambda \) (where \( n = 1,2,3... \)).
Figure 3.2: Energy-momentum dispersion for (a) graphene, and (b) a (5,5) ‘armchair’ nanotube.
Figure 3.2b shows the calculated dispersion relation for an armchair (5,5) nanotube. A smaller area is shown, just bigger than a graphene unit cell. The continuous surface of the graphene dispersion has been broken in one direction, forming several one-dimensional sub-bands. The two metallic sub-bands can be thought of as consisting of a pure bonding and a pure anti-bonding orbitals, while any semiconducting sub-bands are a mixture of the MO's.

The band diagram for any nanotube will look similar. The effect of chirality is to simply rotate the parallel lines of allowed $k$ values relative to the hexagon formed by the K and K' points. Figure 3.3 is commonly used diagram that illustrates this; it is effectively the top view of Figure 3.2. Hence, it is quite possible to produce a circumstance in which no sub-bands pass through a K point. It is this condition that results in a semiconducting nanotube and assuming all chiralities are equally likely in synthesis, two thirds of single wall tubes should be semiconducting, Saito et al (1992). The effect of decreasing the diameter of a tube is to reduce the number of sub-bands in Figure 3.3. In the semiconducting case this means 'on average' the sub-bands will be further away from the K and K' points, referring back to cone shape in Figure 3.2, it should be clear that this would result in a larger band gap.

![Metallic and Semiconducting Band Diagram](image)

**Figure 3.3: The effect of chirality is illustrated by rotating the hexagon formed of the K and K' points**

Small (=2 nm diameter) s-SWNT have typical band gaps = 1.6 eV, comparable to silicon at 1.12 eV. The spacing ($dk$ and hence $\Delta E_{subband}$) of these sub-bands decrease with increasing diameter, reaching an energy separation of 25 meV for a tube of ~40 nm diameter. This band structure of carbon nanotubes as calculated by Satio et al
(1992) has been experimentally confirmed by Wildoer et al (1998) and Odom et al (1998) by atomic resolution scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS). Further use of STS by Lemay et al (2001) imaged the electron wave function within a CNT and confirmed the linear E-k relationship. The density of states (DOS) is shown in Figure 3.4 for metallic and semiconducting tubes along with the more common depiction of the E-k relationship, the k axis corresponding to the propagation constant along the axial direction.

Figure 3.4: Low energy E-k diagrams depicting the 1D sub-bands and the corresponding DOS for a) a metallic tube, with the first semiconducting sub-band shown. b) A semiconducting tube.

3.2 Conduction in Nanotubes – The Issues in Brief

There are a number of inter-twined issues surrounding conduction in nanotubes, reducing it down we want to know: Is conduction ballistic or diffusive? Unfortunately, it is necessary to complicate the picture to get anywhere in answering this question. We need to add some qualifiers:
• Ballistic on the typical length scales of transport experiments, that is 100's of nm to a few microns.

• How do we define Ballistic?
  o Conductance, \( G > 0.5 \, G_0 \) per channel. \( G_0 = \frac{2e^2}{h}, \) and is the expected conductance per spin degenerate channel for a 1D ballistic conductor,
  o With a mean free path (m.f.p.) greater than the conductor length, m.f.p. \( > L_c \), but which m.f.p.? – Momentum relaxation length, \( l_m \), phase relaxation length, \( l_\phi \) or elastic scattering length, \( l_e \)?

Separate to qualifiers above, essentially what controls scattering is disorder and the interaction of electrons with phonons. So we want to know:

• What kind of disorder is present?
• How much disorder can be tolerated?
• What kind of phonons will affect conduction and how?

Feeding into these issues we have the experimental considerations such as, imperfect contacts and substrates (where they are used). With MWNTs we have another big issue, how do the multiple shells effect conduction, how much interplay is there between the shells?

In one-dimensional (1D) conductors electron-electron (e-e) interactions can be very strong, resulting in the breakdown of the Fermi liquid theory (the conventional description of electrons in semiconductors and metals). The effects of e-e interactions can be probed electrically by making a tunnelling contact to the 1D conductor; the resulting behaviour can be explained in terms of theories which assume the conductor to be ballistic or diffusive. The interpretation of measurements of single MWNTs contacted via a tunnelling contact form bulk of the original work in this thesis, so the theories applicable to electrons tunnelling into a MWNT are the most relevant and the end point of this background chapter. In all of the above issues relating to the ballistic or diffusive transport, it is not the case that there are two entrenched opposing schools of thought; rather authors have to go with the interpretation that works best with their observations.
The aim of following sections are to try and gain some answers to the questions surrounding conduction in MWNTs, establish the validity of the assumptions already made (like the separate character of the shells in MWNT) and to set up the reader for a discussion on interpreting the experimental results.

3.3 MWNT Structure, Experimental Conditions and Disorder

3.3.1 Electronic Structure of MWNTs

Perhaps the first thing to do is to demonstrate anisotropy of conduction in MWNTs, and that the individual shells retain there character. By far the best examples of this are the series of experiments conducted by Collins et al (2001), dispersing MWNTs over a substrate with predefined Au/Ti electrodes the MWNTs were pushed to failure. As can be seen from Figure 3.5a, the failure happened in steps. From AFM and SEM the steps corresponded to the failure of individual shells, Figure 3.5b.

Figure 3.5: Reproduced from Collins et al (2001). a) Electrical breakdown of MWNT under constant voltage stress. b) Thinning of a MWNT bridging previously deposited electrodes (250 nm wide) c) and d) low bias conductance – gate voltage, $I_d/V_d$ vs $V_g$.

The voltage stress can be removed after each breakdown step allowing the remaining structure characterised, most significantly for our purpose is the conductance-gate voltage data which shows how the character of each shell is retained. Figure 3.5c shows the $G-V_g$ data for the removal of the first few shells, the outermost shell, $n$ and
next one have been removed, leaving the n-3 shell as the outermost intact shell in Figure 3.5c. The remaining structure appears metallic, as the conductance never drops to zero and has some p-type semiconducting character, i.e. the conductance is enhanced with negative gate voltages. Removal of n-3 shell leaves the remaining structure to behave completely metallic. It is clear that the n-3 shell was semiconducting and the n-4 one was metallic. Further shell removal reveals the last metallic shell is n-9, Figure 3.5d. The inner semiconducting shells have ambipolar characteristics, the conductance is enhanced for positive and negative gate voltages. The increasing in conductance gap, Figure 3.5d, is also just what is expected, the average band gap increases as the diameter of the shell decreases.

The discussion of ballistic or diffusive transport is left for later. However, with regards to the experiments of Collins et al (2001) the conduction cannot be perfectly ballistic. If it was, and only the outer shell contacted, there would be no potential difference along the outer shell, thus there would be no potential difference between the inner shells and the outer one. Therefore, nothing to motivate an inter-shell charge transfer. So we can safely say the conduction was not ballistic in this experiment.

At this point, we should probably elaborate on the experimental methods for the majority of transport measurements on nanotubes, a grouping to that includes the experiments of Collins et al (2001). The standard starting point is a substrate of degenerately doped Si wafer, with a SiO₂ oxide layer which is typically a few hundred nm thick, although sometimes much thinner, ~10 nm oxides are also used. The sequence of events then follows, one of two paths:

1. Deposit nanotube dispersion on the substrate.
2. Locate a suitable nanotube. SEM for MWNTs, for SWNTs; AFM, STM etc.
3. Deposit electrodes. Typically, this done by e-beam lithography and the evaporation or sputtering of a contact metal or pair of metals.

Alternatively, as in Collins et al (2001) the sequence goes 3, 1 and then 2. In any case, the result is a nanotube connected by a number of electrodes and back gate formed by the degenerate Si wafer, Figure 3.6. The key deviations from a theoretical ideal are the presence of a substrate, non-ideal contacts and a Fermi level no longer at the charge neutrality point (where the bands cross). In the following sections, we will see how important these deviations from the ideal are.
3.3.2 Disorder

For any quantum wire, there is a finite amount of disorder present. Even in perfect structures, disorder can be introduced from interaction with the environment. With a long enough sample, this will cause strong localisation, increasing the resistance exponentially with the conductor length, $L_c$. White and Todorov (1998) assessed the impact of residual disorder, by randomly varying parameters of the standard tight binding model of a SWNT. It was found that the free path $l_e$ increased as the diameter was increased, leading to exceptionally long mean free paths, i.e. $>10\ \mu m$. Physically, one can imagine a wave packet delocalised on the circumference but localized on the tube axis, a ‘donut’ shape. Therefore, disorder on the scale of atomic spacing is averaged-out around the whole circumference, as the circumference grows the averaging becomes more effective at minimising the effect of disorder. Additionally, they found that the effect of small bends in the nanotube were compensated for and
would not impact upon $I_e$. Electron-electron interactions are not expected to affect the conclusions.

Long-range disorder cannot be averaged around the circumference. In this situation a disorder potential will interact with the electron and how well long range disorder couples to the low energy scattering processes depends on the initial and final positions of the electron in $k$-space. The dominant factor in the coupling is a cosine $(\frac{1}{2} \theta_{k_i,k_f})$ term, hence, if the argument becomes $\frac{1}{2} \pi$, the coupling will be zero and long range disorder ineffectual.

![Diagram](image_url)

Figure 3.7: (a) Filled states (shaded) in the first Brillouin zone of a single $p$-type graphene sheet. The sheet contains two carbon atoms per unit cell (lower right inset). The dispersions of the states in the vicinity of $E_F$ are cones (upper right inset) whose vertices are located at the K and K' points. The Fermi circle around the K point, the allowed $k$ vectors, and their dispersion are shown in (b) and (c) for a metallic and semiconducting tube, respectively. The dumbbells represent the molecular orbitals comprising the states, with white-white, white-black, and gray dumbbells representing bonding, anti-bonding, and mixed orbitals, respectively. (Figure and caption from McEuen et al 1999)

The angle $\theta_{k_i,k_f}$ is defined in Figure 3.7 as the angle between the vectors, the black arrows form the K point to the Fermi points on the right moving branch ($+dE/dk$) and to the left moving branch ($-dE/dk$). It can be seen from Figure 3.7b that wherever the Fermi points on the metallic sub-bands, the angle between them will always be $\pi$ in the notation of Figure 3.7, the vectors have no $k_y$ component only a $k_z$ component. For
Fermi points in the semiconducting sub-bands, Figure 3.7c, which is displaced laterally from the K point, the vectors will always have a finite $k_y$ component, so $\theta_{k_y} \neq \pi$.

The cosine factor is therefore always zero for the metallic sub-bands forbidding scattering due to long range disorder. On the other hand, for the semiconducting sub-bands, the cosine term is always finite, at it is largest at the opening of the band. The effect of long range disorder was not predicted by McEuen et al (1999), rather this was the first paper to link it with experimental observations.

Consistent with previous measurements, McEuen et al (1999) found that semiconducting SWNTs (s-SWNT) had much lower conductances, $G \ll e^2/h$ whereas m-SWNTs had conductances $\sim e^2/h$. The Coulomb blockade (CB) charging spectra were used to elucidate the cause. CB is described in detail later in section 3.8.1 (p55), but described briefly it occurs when an electron is blocked from tunnelling onto a conducting island because the bias $eV$ or the thermal energy, $k_B T$ is less than the island’s charging energy, $E_C$. The charging energy is inversely related to the size of the island. In the case of metallic tubes the extracted charging energy corresponded to an island equivalent to the tube length, indicating the mean free path, $l_m \sim 8 \mu$m at 1.5 K. While semiconducting tubes displayed a charging energy consistent with $l_m \sim 100$ nm, the s-SWNT was effectively split into five islands between the electrodes in the example given. McEuen et al (1999) concluded that long range disorder, “e.g. localized charges near the tube” broke the s-SWNTs into a series of quantum dots at low temperatures.

McEuen et al (1999) was not the first to have a SWNT sample split into isolated conducting islands, earlier low temperature measurements by Bezryadin et al (1998) showed that as the SWNT followed the contours of the substrate, tunnel barriers resulted. The tunnel barriers caused the CB charging spectra to change from that of a single island, into the more complex charging spectra of several dissimilar islands in series. In this case strong disorder, structural disorder on the scale of the tube size had electrically isolated sections of the tube; this was thought to occur as the SWNTs followed the 15nm step from on top of the electrode to the insulating substrate.

Besides covering the effects of disorder some insight has been gained into the importance of one of the experimental conditions for SWNTs, the substrate; it should
be flat on the scale of tube, i.e. ~ 1 nm and ideally have no trapped charge. This has implications for the choice contacting methodology as well, with the SWNT following every contour of the substrate; draping over thick electrodes is likely to introduce disorder. In response to these results, Cees Dekker’s group at Delft University evolved their experimental set-up such that there was no height difference between the electrodes and the insulating part of the substrate, and the surface roughness was minimised.

The impact of the substrate upon the conduction properties of MWNTs and SWNTs is quite different. As SWNTs are only made from a single graphene sheet, they can deform easily, and will readily do so in order to maximise their adhesion energy. The addition of more shells changes the balance between the energy cost in tube distortions and the surface adhesion energy gained by such distortions (Hertel et al 1998). The many shells of a MWNT give them a rigidity that makes them much less susceptible to variations in the substrate and enables different techniques for electrical measurements. SWNTs do however tolerate gentle bends well, and as discussed by White and Todorov (1998) showed that slight bends do not impact upon the electrical properties. The theoretical work of Rochefort et al (1999) shows as the bend increases to 60°, a buckle will occur. Strong deformations, like buckles cause a mixing or hybridisation of the π and σ orbitals in the vicinity of the deformation, thus modifying the local DOS. These states are more localised and inhibit transmission. An example of this is featured later in section 3.7.1.

Finally, it should be pointed out the metallic sub-bands are not invulnerable to disorder. Bockrath et al (2001) provides a nice example of this with a CVD grown SWNT. Scanned gate microscopy is used to determine that the tube contains two defects. The movable gate allows the resistance contribution of each defect to be isolated (the impact of disorder changes with the Fermi level). The defects had a significant effect, and isolating sections of the tube into quantum dots at low temperature. But, at room temperature the reflection coefficients were 0.5 – 0.7, agreeing well with theoretical estimates for reflection coefficients produced by several atom defects.

In summary, we have covered the impact of disorder on conduction and although an explicit proof of the disorder averaging principle was not featured, the effect is evident in a number of the reports featured in the following sections, notably the room
temperature ballistic conduction in MWNTs. In the same manner, the stark difference between the scattering properties of metallic and semiconducting sub-bands is an aspect of nanotube conduction that will permeate the rest of the literature review.

3.4 Ballistic Conductance

3.4.1 Principals

In ballistic conduction, electrons travel along channels without being scattered. They encounter no resistance within the bulk of the nanotube. This, however, does not mean a nanotube has zero resistance, in fact the resistance or rather the conductance is quantised, into multiples of \( G_0 \), where \( G_0 \) is the conductance per spin degenerate channel:

\[
G_0 = \frac{2e^2}{\hbar}
\]

(1)

This is a simplified version of Landauer’s formula and it equates to a resistance of 12.9 kΩ. It can be arrived at by a number of different methods, a couple are featured here in order to gain a clear insight to ballistic conduction in 1D. Firstly; the approach taken in Saito et al (1998).

![Figure 3.8: Two three-dimensional reservoirs at different chemical potentials are connected by a ballistic conductor of length \( L_C \), the number of ballistic channels available between \( \mu_1 \) and \( \mu_2 \) is \( N \).](image)

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Figure 3.8 depicts ballistic channels. The value of $G_0$ is derived by considering the current in terms of charge per second, using the electron velocity; $I = (e \cdot v_p) / L_c$.

This results in the following expression:

$$I = \frac{e}{L_c} \cdot \frac{L_c}{2 \cdot \pi} \cdot \sum_{k > 0} \frac{1}{\hbar} \cdot \frac{\partial E_j(k)}{\partial k} \cdot \left[ f(E_j - \mu_1) - f(E_j - \mu_2) \right] \cdot dk$$

The expression is formed as follows; a factor of two is added for spin degeneracy. The electron velocity can be determined from $v_p = \frac{\hbar}{m} \cdot (\frac{\partial E}{\partial k})$, which derived from the standard expressions $E = \frac{\hbar^2 \cdot k^2}{2 \cdot m}$ and $E = 1/2 \cdot m \cdot v_p^2$. $f(E)$ is the Fermi-Dirac function. The expression enclosed by square brackets gives the probability that an electron at energy, $E_j$ at contact 1, exists with a smaller probability than an electron at contact 2 with energy $E_j$. The tube has a finite length; hence, $k$ values along the axis are also quantized (need to fit an integer number of wavelengths along the tube axis). Therefore, the minimum value for $k$ is $dk = \frac{(2 \cdot \pi)}{L_c}$, the next allowed $k$ value is $2dk$. Strictly, the velocities should be summed for each allowed $k$ value. However, given the length of our wire, the $dk$ along the tube axis is so much smaller than the actual $k$ values, so the calculation is simplified by approximating the sum to an integral. Since $dk$, has been inserted to the integral, the inverse of the level spacing is also inserted ($\frac{L_c}{(2 \cdot \pi)^2}$). Finally, $N$ is the number of channels and the $\Sigma$ is simply adding the contribution to $I$ from each channel. This all reduces to the expression for $G_0$ above.

However, we will only see a conductance $NG_0$ if the coupling into each channel is perfect, therefore, a transmission coefficient (usually denoted by $T$) is used to account for reflections from imperfect contacts.

While the above explanation seems perfectly reasonable, it doesn't give an easily understood picture of what is conceptually happening. It is hard to gleam from the above equations where the power $(P / G_0)$ is being dissipated, and more fundamentally why is there a finite resistance at all. After all, for ballistic conductance in 2D or 3D there is no such resistance. Answers to these questions can be gained from the transmission line model of ballistic conductance. This model can then easily be extended to include the effects of $e-e$ interactions. The transmission line model for
nanotubes was first used by Bockrath (1999) where the reader is directed for a more thorough treatment.

In a similar manner to Bockrath (1999) we are going to arrive at expressions for quantum capacitance and quantum inductance for a single spinless mode, by considering the potential energy resulting from an increase in the charge density and the kinetic energy stored in a net movement of charge. First the quantum capacitance; Figure 3.9a shows a generic E-k diagram, where the addition of $N$ electrons has increased the Fermi level by $\Delta E_F$. The potential energy ($E_{pot}$) per unit length, $L_C$ can be written as:

$$E_{pot} = \frac{1}{L_C} \int_0^N \frac{1}{2} n \delta n = \frac{1}{4L_C} N^2 \delta$$

(3)

Where, $\delta$ is the energy spacing between allowed $k$ values due to quantization along the wire axis. $\delta$ is given by the product of the E-k gradient and the allowed $k$ value spacing, $\Delta k = 2\pi L_C$.

$$\delta = \frac{dE}{dk} \Delta k = h \nu_F \frac{2\pi}{L_C}$$

(4)

Combining equations (3) and (4) and noting, that $N e / L_C$ can be expressed as the charge density, $\rho$ we arrive at equation (5).

$$E_{pot} = \frac{h}{4e^2} \nu_F \rho^2$$

(5)

Equation (5) is of the same form as the standard expressions for the energy stored in a capacitor, so we can define a quantum capacitance, also sometimes referred to as the compressibility:

$$C_q = \frac{2 \cdot e^2}{h \cdot \nu_F}$$

(6)
Figure 3.9: Reproduced from Bockrath (1999). Generic E-k. a) The addition of electrons to both right and left movers, increasing the potential energy. b) Moving electrons from left propagation to right, i.e. making a current flow, increasing the dynamic energy of the system.

A net current can be made to flow by having more ‘right movers’ than ‘left movers’, this can be seen in Figure 3.9b where two quasi Fermi levels have been set up by taking some left movers and promoting them to right movers. The total energy per unit length is $E_{\text{kin}}$, the number of electrons promoted, $N = (e\Delta\mu/2)\delta$ times the energy gained by each electrons, which is $e\Delta\mu/2$ gives the total energy.

$$L_C \cdot E_{\text{kin}} = \frac{e \cdot \Delta\mu}{2} \cdot \frac{e \cdot \Delta\mu}{2 \cdot \delta}$$ (7)

$E_{\text{kin}}$ can be related to the current by noting that $I = (e^2/h)\times\Delta\mu$ for 1D wires as in Bockrath (1999) or by defining the current $I = Ne\nu/L_C$. In any case one arrives at equation:

$$E_{\text{kin}} = \frac{1}{2} \frac{h}{2v_e e^2} I^2$$ (8)

The form of equation (8) leads to the definition of a kinetic inductance as:
Now that expressions for the capacitance or compressibility, and the kinetic inductance have been established, it is possible to calculate a characteristic impedance for the transmission line, \( Z_{\text{line}} \), given by:

\[
Z_{\text{line}} = \sqrt{\frac{L_{\text{line}}}{C_{\text{line}}}}
\]  

(10)

The admittance should then correspond to the unit of quantized conduction:

\[
Y_{\text{line}} = \sqrt{\frac{C_{Q}}{L_{\text{kin}}}} = \sqrt{\frac{2e^2/hv_{p}}{\hbar/2e^2v_{p}}} = \frac{2e^2}{\hbar} = G_0
\]  

(11)

It is also pertinent to note that the analogy reproduces the Fermi velocity:

\[
v = \sqrt{\frac{1}{L_{\text{kin}}C_{Q}}} = v_{p}
\]  

(12)

At this time, we will try to get answers to the questions posed earlier. Why does 1D ballistic conductance result in quite a large finite resistance? Some authors describe it as a resistance due to the connection of the several modes of a quantum wire to the innumerable modes present in the 3D contacts.

This still feels a little vague though; in fact, the answer lies in Figure 3.9b, and just what happens when a current flows in a 1D ballistic conductor. Looking at the E-k diagram with current flowing (Figure 3.9b), we have an applied voltage \( eV \) equal to the difference in the quasi Fermi levels, which can also be expressed as \( N\delta \), the current, charge per second will be \( Ne \) multiplied by the time taken to traverse the sample, \( v_{p}/L_{C} \).

\[
G = \frac{I}{V} = \frac{N\cdot e \cdot v_{p}}{N\cdot \delta / e} = \frac{N\cdot e \cdot v_{p}}{N\cdot \hbar \cdot v_{p} \cdot 2\pi / e \cdot L_{C}} = \frac{e^2}{\hbar}
\]  

(13)

It takes a lot of voltage to move a small amount of charge, i.e. when a current flows there is a significant disturbance to Fermi points. In higher dimensions, to get the same current flowing the disturbance to the Fermi line, or Fermi surface is much smaller. So it can be seen the resistance results from the low carrier density in 1D.
3.4.2 Observations

Despite the relative complexity of MWNTs compared to SWNTs, it is the more complex MWNTs that have provided the best demonstration of ballistic conductance. The seminal work in this area is that of the deHeer group (Frank et al 1998). The experiment consisted of dipping pieces of the carbon electrode tips used in the arc discharge method of MWNT synthesis into liquid mercury (Figure 3.10a). The pieces from the carbon electrode are covered in MWNTs, and amorphous carbon, with often a single tube protruding beyond all others. So when it is lowered towards the liquid metal (mercury) contact, a two terminal IV measurement of a single freestanding MWNT can be made.

Figure 3.10: Reproduced from Poncharal et al (1999). a) TEM of a MWNT approaching the Hg contact. b) Conductance with depth from the SPM set-up, the additional steps corresponding to more MWNTs contacting the Hg.

Initially the experiments were conducted in air, at room temperature with a modified scanning probe microscope (SPM), and then later the same experiment was conducted in a transmission electron microscope (TEM). Repeated dipping had the effect of cleaning much of the carbon debris left from the arc discharge process. After this, conductance measurements showed clear plateaus with steps of conductance (~0.9G₀), were consistently observed, see Figure 3.10b.

Between the top contact and the furthermost protruding MWNT there will be a complex network of tubes and carbon debris. Poncharal et al (2002) attributed the missing conductance to the relatively poor transparency of this connection. Several others independently proposed their own explanation for the ‘missing’ conductance but when later Urbina et al (2003) demonstrated a conductance of 2G₀ with a similar experiment, the original, simple explanation in Poncharal et al (2002) seemed by far...
the most credible. The measurements of Urbina et al (2003) were conducted on freestanding arc-discharge produced MWNTs over distances of at least 1.4 μm. The measurement was carried out by engineering a solution which contains MWNTs and spin coating it onto a Au substrate. A SPM tip is then lower into the solution as the tip is retracted MWNT(s) initially stick to the tip. Integer multiples of 2\(G_0\) conductance are always observed between the Au substrate and the SPM tip.

Besides measuring the conductance as \(V \to 0\), Frank et al (1998) were able to measure the conductance up to ~ 6V, after which the MWNT failed. At this point the power dissipated was ~ 3 mW. Conducting the experiment in the TEM Poncharal et al (2002) was able to show a pristine MWNT before and after failure, Figure 3.11. The outer shell is completely destroyed, in keeping with ballistic conductance in the outer shell only.

![Figure 3.11: Reproduced from Poncharal et al (2002) TEM of the before (a) and after (b) failure of a pristine MNWT. Only the outer shell is damaged.](image)

The conductance voltage characteristic further supports ballistic conductance in the outer shell only, Figure 3.12a. After a plateau with a width that corresponds to the band gap of the first semiconducting sub band, the conductance increases linearly with voltage. The linear increase corresponds to an increasing participation of the semiconducting sub-bands. The linear \(GV\) characteristic is a temperature smoothed staircase, the height of each step being dependant on the contact and transparency and the transparency of the 1D channel, \(dG = 2G_0 \times T_{contact} \times T_{semi\ sub\ band}\). The width, \(dV\) is
dependant on the sub-band separation, which is inversely proportional to the tube diameter.

![Graph](image)

**Figure 3.12:** a) Reproduced from Poncharal et al (1999); typical conductance voltage characteristic. The solid line is from the SPM setup with a gradient of 0.25 \( G_0 V^{-1} \), open circles from a tube in the TEM setup 0.5 \( G_0 V^{-1} \). b) Reproduced from Poncharal et al (2002), the same measurement conducted on a tube dipped in sodium dodecyl sulfate (SDS) suspension fluid.

With sub-band separations in typical MWNTs around 100 meV and the conductance only doubling after 4 V (Figure 3.12a), the height of each step is \( << 2G_0 \) meaning in the semiconducting bands the transmission coefficient is very small, \( T_{\text{semi subband}} = 0.02-0.03 \) (Poncharal et al 2002). Providing a clear example of the different properties of semiconducting and metallic sub-bands as discussed previously in 3.3.2.

Others such as Liang et al (2004) have made similar observations (Figure 3.13), in different geometries, where the dissipation of heat is more efficient allowing for an exploration of the GV characteristic to higher voltages. The conductance saturates when all sub-bands are participating, i.e. run out of the energy range of \( \pi \) and \( \pi^* \) bands.
Figure 3.13: From Liang et al (2004), Measured $IV$ characteristic (right axis) and the conductance, left axis. Inset shows schematic diagram of experimental set-up.

Figure 3.12b shows the same $GV$ measurement on a sample that has been dipped into SDS suspension fluid. SDS is commonly used when dispersing nanotubes over a substrate. Poncharal et al (2002) did this to check if it was the condition of the MWNT that could account for the stark differences between the experiments that revealed MWNTs to be ballistic conductors at room temperature and those experiments in which MWNTs displayed diffusive conductance even at low temperatures. The $GV$ characteristic in Figure 3.12b clearly deviates significantly from Figure 3.12a, the ballistic case, adding considerable weight to the arguments of Poncharal et al (2002), that the standard techniques employed in on-substrate experiments can destroy the ballistic conduction.

The measurements of Urbina et al (2003), which revealed $2G_0$ conductance were with electrode spacing of $\sim 1.4 \, \mu m$, so it was concluded $l_m \geq 1.4 \, \mu m$ at room temperature for MWNTs. The electrode separations were of a similar scale in the experiments of Poncharal et al (2002), but the ability to change the contact length and electrode spacing allowed the free path to be extracted. Poncharal et al (2002) determined $l_m \sim 200 \, \mu m$ at room temperature.
Many of the experimental techniques that have revealed ballistic conductance in MWNTs are not transferable to SWNTs, mostly because of the rigidity and larger diameters of MWNTs. Hence, there are no such experiment measuring 100s of different tubes and finding the conductance to always be $2G_0$ or $0.9 - 1G_0$ for SWNTs. There are some papers which describe conductance to be ballistic based on the value of conductance, Krstić et al (2000) finds a two terminal resistance of $2G_0^{-1}$ (with a 100 nm electrode separation) after adjusting for a lead resistance of the same order. The measurements reported by Krstić et al (2000) were actually done with three terminals and it was concluded that the SWNT could be ballistic conductors on the scale of 300 nm at room temperature.

The Palladium (Pd) contacts used by Mann et al (2003) consistently gave very high two terminal conductances, ~ $1.5G_0$, for metallic SWNTs. With longer samples (4 μm) this conductance is only seen at low temperatures (4 K). The shorter samples showed quite high conductance, $1.25G_0$ at room temperature and clean Fabry-Perot interference patterns at low temperatures consistent with a resonator of equal length to the electrode spacing as originally described by Liang et al (2001). Mann et al (2003) concluded that the mean free path for acoustic phonon scattering is around 500 nm at room temperature and > 4 μm at low temperatures for metallic tubes. It could indeed be much greater as previously discussed by McEuen et al (1999) who found, $l_m$ ~ 8 μm at 1.5 K in a metallic tube.

A particularly clear demonstration of ballistic conductance in a SWNT at room temperature was provided by Bachtold et al (2000), where the potential drop along the tube was directly imaged with electrostatic force microscope (EFM), an AFM hybrid. The resulting ‘voltage map’ showed that the voltage was dropped at the ends of the nanotube near the contact; almost no voltage was dropped along the length of the tube (>1 μm). The extracted transmission coefficient within the tube was > 0.5, a benchmark for ballistic conductance.

There is also another class of experimental evidence for ballistic conductance in metallic SWNTs. Ballistic transport is a prerequisite for the formation of a Luttinger liquid (LL) state and later in section 3.7, evidence for an LL state in SWNT will be presented.
3.4.3 Summary

There seems to be no doubt that ballistic conduction in MWNTs is routinely achieved at room temperature over micron distances. Although a mean free path of 200 µm was extracted in the Hg contact experiments, many would only be convinced of ballistic transport over that kind of distance when an experiment is conducted with an electrode spacing of this order. Ballistic conductance is also well established in SWNTs, especially at low temperatures. The room temperature mean free paths seem to be a little smaller than those observed for MWNTs, a few hundred nm is typical.

With regards to the importance of the experimental conditions, it has been shown that near perfect contacts are achievable, e.g. the $2G_0$ values observed by Urbina et al (2003). Routinely achieving equivalent contacts for SWNT is much tougher, but techniques such as EFM allow the demonstration of ballistic conductance regardless of contact transparency.

Poncharal et al (2002) showed that the condition of the nanotube is critical to the observation of ballistic conductance, with MWNTs dipped in SDS failing to show ballistic transport. The nanotube condition or more importantly, possible surfactants on the nanotube such as SDS, are critical issues in the argument over whether conduction is diffusive or ballistic in MWNTs.

3.5 Inter-Shell Conductance

Bourlon et al (2004) was the first to experimentally quantify the intershell conductance. There were of course indications of the high anisotropy in the conductivity of MWNTs, such as the work featured in section 3.3.1. The results gained by Collins et al (2001) are unlikely to have been the same if MWNTs were isotopic conductors. Also, a study featured in the previous section, 3.4.2 showed the failure of the outer shell only in the case of ballistic conduction, again indicating current flow is not evenly distributed within the shells.

Theoretical studies flourished in the experimental void before 2004. A direct quote from Bourlon et al (2004) highlights two of the extremes. “For example, zero intershell transport is predicted for an infinitely long and perfect tube, since both the energy and the Bloch wave vector have to be conserved (Yoon et al, 2002). In contrast, it has been shown that the intershell transmission is large when electrons are
injected as localized wave packets from outside the shell (Roche et al 2001). The attenuation length, which is the length necessary for a charge flowing along a shell to propagate into the next shell, was found to be very short, 1–10 nm.”

Figure 3.14: Probe configurations a) Measurement of local voltage, typical 4 point probe set-up. b) and c) measurement of non-local voltage.

Four point probe measurements are usually made by driving current between two electrodes and monitoring the voltage with a pair of probes whose location could be in between the current probes (Figure 3.14a) or outside of them. The voltage difference is called the local voltage. To get quantitative information on the anisotropy of the current flow, Bourlon et al (2004) monitored the non-local voltage (Figure 3.14b). A voltage between two points where no current is expected to flow for a perfectly isotropic material. With, a probe configuration set up to monitor the non-local voltage and 11 contacts to a single MWNT, variations on the spacing of both pairs of probes allows the anisotropy to be characterised, (e.g. Figure 3.14c).

Bourlon et al (2004) found the resistivity for the outer shell, n to between 6 to 25 kΩ/μm. The important findings are: -

- **Intra-shell transport is more efficient in the n-1 shell**: The relative resistivity of the n-1 shell showed considerable variation between 2 to 0.05 times the resistivity of the outer shell, but it was most often found to be lower. Despite the random character (semiconducting or metallic) of the n and n-1 shells, the n-1 shell most often has a lower resistance, therefore surfactants on and/or any damage sustained on the outer shell may affect the transport on the outermost shell but inner shells appear to be less affected.

- **The shells are well insulated from each other**: The inter-shell conductance was found to be 3.7 to 20 kΩ⁻¹/μm and displayed no strong temperature dependence. The strong variation in inter-shell resistivity along the same tubes could be attributed to the inter-shell conduction mechanism being dependant on defects and inhomogeneities. Although Bourlon et al (2004) gained
quantitative agreement by considering tunnelling conductance of the π-orbital overlap between two atoms of neighbouring shells, the dominant mechanisms for inter-shell charge transfer is not known.

- **The end cap does not play a role in inter-shell conductance**: the non-local voltage at the end (far away from the current contacts) was zero.

Interlayer defects which might play a role in the intra and inter-layer conductivity have been directly observed by TEM within DWNTs by Urita et al (2005). The defects are caused by the high energy electron bombardment; they can be described as stable for a macroscopic time at room temperature; above ~ 450 – 500 K any defect appears to heal very quickly.

### 3.6 Diffusive Conduction in MWNTs

Just as the EFM experiments of Bachtold et al (2000) provided a clear evidence of ballistic conduction in SWNTs (section 3.4.2), the same experiment on MWNTs showed charge transport was diffusive, as a potential drop was observed along the tube length. With a bias of 0.15 V, a resistance of 10 kΩ/μm was extracted.

In terms of a room temperature resistance per micron, this is fairly typical, (see Table 5.3, for more values). Extracting more than just a resistance per micron and a maximum possible current is quite difficult with room temperature IV measurements alone. The experiments of Collins et al (2001) being a notable exception and it is this technique which provides a model for high bias conduction in MWNTs.

The usual tools for determining conduction mechanisms have of course been applied to MWNTs on substrates, namely cooling down to low temperatures and high magnetic fields. Schönenberger et al (1999) reports extensively on these methods in an attempt to provide some solid answers concerning conduction in MWNTs. The experiments with magnetic fields, both parallel and perpendicular to the MWNT axis, have been interpreted with weak localisation (WL) theory.

Weak localisation increases resistance, above the normal diffusive case. If an electron is elastically scattered, it may return along the same path it came (a time reversed trajectory). This results in the ‘scattered’ portion of the electron wave interfering with the remaining ‘yet to be scattered’ part, as it returns along the same path. The electron interferes constructively with itself creating a larger, enhanced wave function. This is
then more likely to scatter other electrons that encounter it. This is why WL is often described as creating an enhanced backscattering potential. Applying a magnetic field causes changes in the phase shift of the scattered electron wave function, reducing the constructive interference and therefore the scattering potential. Thus, for WL negative magnetoresistance is observed, the resistance decreases on the application of a B field (decreasing by 20% from B = 0 to B = 3T).

With the application of a perpendicular magnetic field the MWNT resistance was found to decrease as expected for WL. Only 1D WL could be made to fit the results. 2D and 3D forms of WL did not fit the data. Therefore, the phase relaxation length should be at least the circumference, \( l_\varphi \geq 2\pi r_{\text{int}} \). In fact, \( l_\varphi \) was extracted to be a few hundred nm at low temperature, extrapolating the trend in \( l_\varphi \) vs. \( T \) to room temperature, \( l_\varphi \sim 60 \) nm.

Application of a parallel B field to the axis of a MWNT results in the Aharonov-Bohm effect, which is a periodic variation of resistance of a thin walled cylinder (unlike the monotonic decrease in resistance for the perpendicular B field case). The period of the oscillation is related to flux through the cylinder. The peak resistance is at \( B = 0 \); has an origin that is the same as that of WL, except here an electron interferes with its time reversed path around the circumference of the cylinder. 

Bachtold et al (1999) observed this effect in MWNTs, the measurement implied that the current was carried in the outer shell only, or at most two layers. The very effect also implies that the conduction is diffusive, with \( l_\varphi \sim 2\pi r_{\text{int}} \). The period of the oscillations in resistance with B field agrees well with the diameter of the MWNT, and not the average diameter of all shells, indicating the current is carried in the outermost shell or two shells at most. However, smaller periodic fluctuations were also observed super imposed on the main oscillation. These are expected for electrons traversing the circumference several times. What was unusual and unexplained was that the best data was obtained from fitting \( n = 1 \) and \( n = 10 \), rather than a wider spectrum of n. An electron travelling around the circumference 10 times would imply \( l_\varphi = 250 \) nm.

A mean free path can also be extracted from the absolute resistance values by modelling the diffusive conduction with a Drude equation. Here, the only source of scattering is disorder. Assuming conduction was two dimensional failed, a mean free
path, $l_e \sim 13$ $\mu$m was found, violating the diffusive assumption as well as the 2D assumption. With 1D diffusive conduction, a more reasonable value of $l_e$ was extracted, 50 nm. The Drude equation is a simple approach, as it takes account of no temperature dependant scattering mechanisms, therefore $R(T)$ is expected to be constant. $R(T)$ was not constant, nor could it be explained with WL. Before and after corrections for WL, power law behaviour was observed. This portion of Schönenberger et al (1999) results is discussed later in section 3.9.1.

Finally, we state that one of the samples in the investigations of Schönenberger et al (1999) exhibited a high resistance contact. Normally, a contact resistance of $R_c << 10$ k$\Omega$ was achieved on all four connections. The high resistance tunnel contact allowed the DOS to be probed, as $dI/dV \propto$ DOS for a tunnelling contact. The $dI/dV$ showed clear Van Hove singularities, 1D-DOS signatures, indicating once more that $l_e \geq 2\pi\epsilon_{\text{cutoff}}$. In fact the broadening of the Van Hove singularities gave $l_e \leq 150$ nm.

Summarising the low temperature results, four mean free paths extracted by Schönenberger et al (1999) have been featured here. What has emerged is not exactly a consistent story, even within the diffusive conduction picture. Not all the results can be interpreted within a structure that has the same dimensionality. The best consensus that can be extracted is: the mean free path is on the scale of the circumference, not much bigger and not much smaller, implying $l \sim 60 - 100$ nm, and that the current is carried in the outer one or two shells at most.

It is difficult to discuss diffusive conduction in nanotubes further without introducing phonons, the last of the scattering mechanisms laid out in section 3.2.

### 3.6.1 Role of Phonons

There are two classes of phonons, optical and acoustic. Acoustic phonons have typically long wavelengths (relative to atomic spacing). Optical phonons have short wavelengths (again relative to atomic spacing) and hence have higher energy ($h\Omega$), with $\Omega$ being the phonon frequency.

The vibrational displacement can be in the direction of the wave's propagation (longitudinal) or normal to the direction of propagation (transverse), leading to the short hand: LO for longitudinal optical, LA for longitudinal acoustic etc. The unusual structure of nanotubes also gives rise to some other phonons, with descriptive names;
‘twistons’ a kind of transverse acoustic phonon where the displacement can be considered the degree of twist placed on the tube and the radial breathing modes are important for small diameter SWNTs.

Figure 3.15 shows the electron-phonon backscattering processes. Phonons can significantly change the electron’s momentum \( \langle k \rangle \), or energy or both. In the case of zone boundary optical phonons, backscattering an electron from the vicinity of one K point to the other in the Brillouin zone.

![Diagram](image)

**Figure 3.15:** Reproduced from Park *et al* (2004). “Diagrams showing electron-phonon scattering in a metallic SWNT by phonons with energy \( \hbar \Omega \) that satisfies energy and momentum conservation. (a) Emission and absorption of an acoustic phonon with low energy and small momentum. (b) Emission of an optical phonon (high energy and small momentum) and (c) a zone-boundary phonon (high energy and large momentum).”

In much the same way as electrons in a crystal lattice, phonons also have an \( E-k \) dispersion relation. Just as the Fermi level determines how the electron \( E-k \) dispersion is occupied or populated, the temperature determines what part of the phonon dispersion is populated, for example it is unlikely to find a phonon whose energy \( \hbar \Omega \gg k_B T \).

### 3.6.1.1 SWNTs

Yao *et al* (2000) were the first to observe the saturation of current in carbon nanotubes, and broadly speaking the explanation has remained since. Using metallic SWNTs to which low contact resistances were achieved, the current was seen to saturate at high bias, Figure 3.17, with a value of current > 20 \( \mu A \) at 5 V. This was found to be almost independent of electrode separation (19 - 23 \( \mu A \), 700 nm to 2 \( \mu m \)). The proposed explanation for this universal saturation of current was the emission of optical or zone boundary phonons with energy, \( \hbar \Omega = 0.16 \) eV. As can be seen from
the lower inset of Figure 3.17, the IV is characterised by a linearly increasing resistance with voltage. Figure 3.17 is actually the simulated results, but they do agree very well with the experimental data. The simulated results were gained from solving the Boltzmann transport equation. Such good agreement was achieved via the condition, \( l_\Omega >> l_{op} \). The condition is: the distance required for an electron to gain enough energy to emit a phonon is much greater than the mean free path, after that point. The electron phonon coupling is very strong. Electrons lose their energy very quickly after gaining enough energy to emit an optical or zone boundary phonon, (upper inset in Figure 3.17).

\[ l_\Omega \]

\[ l_{op} \]

\[ \hbar \Omega \]

\[ -eE \]

\[ \nu \]

Figure 3.16: A modified reproduction of a diagram appearing in Park et al (2004). \( l_\Omega \) is the distance required to gain energy \( \hbar \Omega \) from the electric field, \( E \) and \( l_{op} \) the mean free path based on the interaction strength of electrons and optical phonons.

As can be seen from Figure 3.16, the distance required for an electron to gain energy \( \hbar \Omega \) is:

\[
I_n = \frac{\hbar \cdot \Omega \cdot L_c}{e \cdot V_{bias}} = \frac{\hbar \cdot \Omega}{e \cdot E}
\]

(14)

Where, \( E \) is the electric field strength. At 5 V, \( I_\Omega \) is just a few tens of nm.
Figure 3.17: Reproduced from Yao et al (2000). Numerical calculation of SWNT IV characteristic (in excellent agreement with measurement). Upper inset shows phonon emission when the difference in the quasi Fermi levels reaches $\hbar \Omega$. Lower inset shows the form of the IV is well characterised by a resistance linearly increasing with voltage.

Further exploration of the current saturation by Javey et al (2004) and Park et al (2004), ranging to smaller electrode separations than those used by Yao et al (2000), showed that in fact, the current does not saturate with small electrode spacing, but instead an increased resistance is seen, Figure 3.18.
Figure 3.18: Reproduced from Park et al (2004). The CVD grown SWNTs are contacted by Au electrodes at each end and an AFM tip is used as a third electrode.

Using a Landauer formula approach a m.f.p. can be extracted from the slope of the IV characteristic. From the slope, at low voltages Park et al (2004) extracts a room temperature free path of \( l \approx 1.6 \mu m \). This compares well to the calculated value of 2.4 \( \mu m \) for \( l_{ap} \), the m.f.p. due to acoustic phonons. The discrepancy is ascribed to \( l_{ap} \) not accounting for any backscattering due to disorder.

Turning to the high bias characteristics, earlier it was not clearly argued why the current saturates. This is done here where the absence of current saturation in samples with \( L_c \leq 200-300 \text{ nm} \) can also be addressed. Essentially, the current saturates when the dominant contribution to the m.f.p. is optical or zone boundary phonons, and within this condition it is when \( l_{\Omega} \gg l_{ap} \), i.e. \( l = (l_{ap} + l_{\Omega}) - l_{\Omega} \). From equation (14) it can be seen that the m.f.p., \( l \) is now inversely proportional to the bias voltage, \( l \propto V_{bias}^{-1} \). Therefore, as \( V_{bias} \) increases, \( l \) decreases, increasing the resistance, leading to a saturation current (Park et al 2004):

\[
I_{sat} = \left( \frac{4e}{h} \right) \cdot h\Omega
\]

The current will not saturate when the length, \( L_c \) is short such that \( l_{\Omega} \ll l_{ap} \) in this condition. The m.f.p., \( l \sim l_{ap} \) which is voltage independent, hence the high bias resistance is voltage independent, and there will be no saturation. From the high
voltage slope of short segments Park et al (2004) extract a m.f.p. of 10 nm. This compares reasonably well to the calculated m.f.p. of \( l_{op} = 180 \) nm and \( l_{zp} = 37 \) for the optical and zone boundary phonons, \( l^{-1} = \frac{1}{l_{op}^{-1}} + \frac{1}{l_{zp}^{-1}} \), \( l \sim 30 \) nm (Park et al 2004). Javey et al (2004) get very similar results with two terminal measurements using Pd contacts (near ohmic contacts). \( l_{op} \sim 300 \) nm and \( l_{zp} \sim 15 \) nm, both from data fitting as in Park et al (2004), and theoretical analysis. Both Javey et al (2004) and Park et al (2004) extracted optical or zone boundary phonon m.f.p. using the Landauer formula approach. Javey et al (2004) also employed a sophisticated Boltzmann equation approach, although the m.f.p. was a fitting parameter in this particular methodology. Park et al (2004) used a tight binding approach to independently generate \( l_{op} \) and \( l_{zp} \), although as Lazzeri et al (2005) points out, that the m.f.p. generated from the tight binding approach has an order of magnitude variation.

Lazzeri et al (2005) argue that the m.f.p. extracted from the experiments are surprisingly small. Their own approach (density functional theory, DFT) for calculating the electron phonon coupling does not use tight binding models and has been validated on graphene. The electron phonon coupling together with the phonon population gives the m.f.p., which is of the order of 100 nm at room temperature, assuming the phonon occupation is thermalized at room temperature (an assumption also made in all of the experimental papers featured here). The ~10-nm m.f.p. extracted from experiments can only be reconciled with theoretical estimates of the m.f.p if the assumption of thermalized phonon occupation is incorrect. If the occupation of the optical phonon states is much higher than expected at room temperature, phonon absorption also becomes a relevant process, as well as phonon emission. In order to reconcile the m.f.p. the phonon population has to be equivalent to a temperature of 6,000 K: This can only happen if phonon emission occurs at a faster rate than the phonons can be thermalized to the lattice, whose temperature is around 300 K. The phonon temperature will increase until the rate at which phonons are created is equal to that at which they are thermalized. But, clearly the lattice temperature is not 6000 K, as the SWNT would melt if so.

The overall picture appears to be of acoustic phonons dominating transport at low bias, giving long mean free paths. \( l_{op} \) is typically a few hundred nm to a over a micron (Javey et al 2004 and Park et al 2004). At high bias (\( \geq 0.2 \) V), optical or zone boundary phonons are dominant. They are generated faster, and then they can be
thermalized to the lattice temperature such that phonon absorption becomes a relevant process, reducing $l_{op}$ from $\sim 100$ nm to $\sim 10$ nm.

3.6.1.2 MWNTs

Much of the experimental and theoretical work has naturally focused on SWNTs. They are of course simpler systems to confidently understand and model, as there can be many unknowns with MWNTs. Additionally, knowledge of phonons in SWNTs is important for applications like transistors. However, significant progress has been made in understanding MWNTs too. Current saturation in MWNTs was also observed by Collins et al (2001) (section 3.3.1), and at that time it was simply concluded it was “similar to that observed in individual SWNTs (Yao et al 2000)”.

It could be said that Bourlon et al (2004) continued the work of Collins et al (2001) featured in section 3.3.1. Collins et al (2001) presented a simple picture of the failure of each shell corresponding to a uniform step or jump in current of $\Delta I \sim 19$ $\mu$A, but $\Delta I$ is actually reported to be different in the later publications, $\Delta I \sim 12$ $\mu$A (Collins et al 2002). It can even be seen in Figure 3.5a that $\Delta I$ is not quite 19 $\mu$A for the last steps shown. Essentially, Bourlon et al (2004) carried out a detailed study of MWNT under high bias conduction with the shell breakdown technique. Using different electrode spacing on the same MWNT, the more subtle features of shell breakdown were elucidated, enabling the construction of a model for MWNT conduction at high bias, building upon the phonon work in SWNTs. Some of the import observations were:

- $\Delta I$ has a weak dependence on diameter (large diameter, large $\Delta I$). There is a clear relationship in short segments (200 nm electrode separation), but for longer separation (650 nm), it is only just discernable.

- The last few shells often fail together; the number of ‘the last few’ is greater when the electrode spacing is greater.

- It appears not all shells participate; extrapolating $I_{sat}$ vs. $r_{out}$ does not lead to $I_{sat} \sim 25$ $\mu$A for $r_{out} \sim 0.7$ nm i.e. what is observed for SWNTs. In fact at $r_{out} \sim 0.7$ nm the predicted current is negative.

All of these features and others were explained in high bias model of conduction in MWNTs that featured two components, the saturation of current due to emission of an
optical or zone boundary phonon, just as in Yao et al (2000) and Zener (inter sub-band) tunnelling.

![Figure 3.19: Reproduced from Bourlon et al (2004). “Schematic of the potential variation in space.” The boxes show the E-k diagram for the semiconducting shell. The dark grey triangle shows the shape of the Zener tunnelling barrier.](image)

Given that the initial calculations show that $\hbar\Omega$ is not dependant on $r_{cm}$, it falls on Zener tunnelling to explain the observations. The current is calculated using the Landauer formula. It is a simpler approach, less accurate than a model based on the Boltzmann equation as employed by others, e.g. Yao et al (2000). Nevertheless, it is remarkably successful in explaining the experimental observations. The Landauer formula takes in the transmission coefficients due to the emission of phonon, $T_{ph}$, and the transmission coefficient due to Zener tunnelling, $T_z$. The behaviour can be explained from the relative size of these coefficients in any one circumstance.

$T_{ph}$ has no diameter dependence and is 0.045 at 3.5 V. However, it can be seen from Figure 3.19 that $T_z$ will have a diameter and length dependence, the barrier (grey triangle) becomes higher for small diameter tubes, while for longer electrode spacing the barrier length becomes greater (relative to a shorter section with the same bias voltage). In 15 nm diameter, 200 nm long section, $T_z$ is calculated to be $\sim 0.7$, so $T_z > T_{ph}$, and the current is limited by phonon emission. The experimental observations can therefore be explained:

- For small diameter shells, 3 nm $T_z \sim 10^{-4}$, $T_z < T_{ph}$ and the current is limited by Zener tunnelling. This explains the diameter dependence of $\Delta I$. 

- 45 -
• The observation of the last few shells typically failing together is explained by the outermost intact shell being semiconducting, and therefore carrying little current given its small diameter. Most current is carried by inner shells, protected from oxygen by an intact outer layer, the eventual failure is catastrophic. The ‘last few’ consisting of more shells in longer segments is because the length dependence of $T_Z$ makes an intact outermost semiconducting shell effectively insulating at larger diameters, when the electrode separation is greater.

• In answer to the final example of the experimental observations of Bourlon et al. (2004) that were featured earlier; it has already been shown that small diameter semiconducting shells do not contribute greatly to the saturated current.

Another important result from the calculation of $T_Z$ is that, $T_Z$ is essentially small for tunnelling processes outside of the depicted situation in Figure 3.19, which shows tunnelling occurring from the highest valance sub-band to the lowest conduction sub-band.

That last result leads directly into the summary of diffusive conductance in MWNTs. At high bias, current saturates for the same reason as it does in SWNTs. The emission of optical or zone boundary phonons. In high bias regime current is predominately located in just a few sub-bands of each shell. At low bias, conduction occurs within several modes of the outer one or two shells, with the m.f.p, $l \geq 2\pi r_{\text{int}}$.

### 3.7 Luttinger Liquid Theory and Electron-Electron Interactions in SWNTs

This section is intended to introduce a Tomonaga-Luttinger Liquid state, commonly referred to as a Luttinger Liquid (LL), how it is applied to SWNTs and to describe some of its characteristics. In sub-sections 3.7.1 and 3.7.2, evidence for a LL state in SWNTs is shown, evidence for a LL state in MWNTs is presented in section 3.9. Fisher and Glazman (1997) provide a review of theoretical progress in the field, while more recent nanotube specific LL reviews can be found in Bockrath (1999), and Burke (2002).
Fermi-liquid (FL) theory successfully describes the behaviour of charge in many metals and semiconductors in two and three dimensions. It uses quasi particles to describe the ground state and low-level excitations. These quasi particles aren't exactly individual electrons or holes, but for most purposes this approximation is acceptable. In one dimension, it is no longer reasonable to treat electrons as independent quasi particles. Electron-electron interactions, that is the repulsive Coulomb forces between electrons become significant. This is because charge is only free to move in one dimension: Whereas electrostatic fields remain free to vary in three dimensions. The interactions tie the electrons together, creating a collective state.

One way to understand how this will alter the electron's behaviour is to make use of the analogy commonly used for phonons. That is to say, lattice atoms are masses connected to each other by springs. In a LL, the electrons act as masses and the springs formed are due to Coulomb and Pauli forces (Figure 3.20). In this manner it is much easier to imagine how a perturbation on one electron impacts upon the others. The hardness or strength of the springs corresponds to the strength of the interactions, with the Luttinger parameter, $g$, characterising the interaction strength. $g = 1$ corresponding to no interaction (Fermi liquid behaviour), while $g < 1$ corresponds to repulsive interactions, as $g \rightarrow 0$ the interactions become stronger.

![Electrons connected by springs](image)

**Figure 3.20:** Mass and spring analogy applied to Luttinger liquids, the compressed springs form represent the repulsive Coulomb and Pauli forces between the electrons.

The process of adding an electron into a LL can be qualitatively understood using the mass and spring analogy. If we keep the length of the chain the same and place another mass in the chain, the action of squeezing the mass in will send waves along the chain, and it will take some energy to do this. What this amounts to is a modification to the wave function of every electron in the LL.

However, this is a rather basic picture. A more accurate picture of the process of adding an electron into a LL can be gained from picturing the local charge density as an additional electron is created in the LL. Initially the charge density is constant.
Within the LL, when an electron enters the LL the local charge density is distorted as shown in Figure 3.21.

![Figure 3.21: Reproduced from Bockrath (1999). “A fast tunnelling step through the barrier adds an electron and creates a local deformation in the charge density [$\rho$]. At zero energy, this configuration is classically forbidden.”](image)

The deformation of $\rho$ at the end of the semi-infinite LL, ($x = 0$) is a sudden perturbation to the LL, introducing anharmonics into the plasmon spectrum: These anharmonic terms make up the deformation in $\rho$. The anharmonic terms decay over time leaving only harmonic terms as the LL returns to its ground state.

The transmission line theory presented in section 3.4.1 can now be extended to cope with the electron interactions just as in Bockrath (1999). $e$-$e$ interactions represent an additional potential energy cost when increasing the local charge density, $\rho$. The additional potential energy stored in the Coulomb forces effectively places a self-capacitance, or electrostatic in series with the quantum capacitance, $C_Q$. Such that with $e$-$e$ interactions the potential energy, (originally defined in equation (5)) can be redefined as:

$$E_{pot} = \frac{\rho^2}{2C_Q} + \frac{\rho^2}{2C_{ES}}$$

(16)

Where $C_{ES}$ is the electrostatic capacitance. The reduction in the total capacitance increases the plasmon velocity:
$$v_p = \sqrt{\frac{1}{L_{slm} \cdot C_{ES}} + \frac{1}{L_{slm} \cdot C_Q}}$$ \hspace{1cm} (17)

This leads on to a quantitative definition for the interaction strength:

$$g = \frac{\nu_E}{\nu_p} = \left(1 + \frac{C_Q}{C_{ES}}\right)^{-\frac{1}{2}}$$ \hspace{1cm} (18)

Earlier, the idea that interactions tie all the electrons together into a single correlated state was introduced. The addition of a single electron disturbs this state. In fact it creates an infinite number of 1D plasmons within the LL. Having now looked at the strength of the interactions we are in a position to expand, quantitatively on the idea that the disturbance caused by a tunnelling electron has an energy cost associated with it. The energy cost manifests itself in altering the TDOS \(\nu(E)\) in power law form:

$$\frac{\nu(E)}{\nu_0} \propto |E - E_F|^\alpha$$ \hspace{1cm} (19)

Where the ‘original’, non-interacting TDOS is given by \(\nu_0\), and the exponent, \(\alpha\) is related to Luttinger parameter, \(g\) and the tunnel electrode geometry. The normalised interacting TDOS is suppressed as a power law. The origin of the power law comes from a full quantum mechanical treatment of the tunnelling event which can be found in Bockrath (1999).

So far, the description has been of a quantum wire with a single, spinless mode and it has not really been shown how it quantitatively relates to a SWNT and any experimentally observable quantities.

Firstly, the capacitance terms. A metallic nanotube has four conducting modes at the Fermi level, two sub-bands, each with spin degeneracy of two. So the quantum capacitance, \(C_Q\) should include a factor of 4, i.e. the quantum capacitance for each mode goes in parallel. This total quantum capacitance goes in series with one electrostatic capacitance, \(C_{ES}\). In the usual experimental configurations for measuring nanotubes, the SWNTs are dispersed on an oxidised Si wafer (see Figure 3.6). The degenerate Si beneath the SiO\(_2\) acts as a ground plane. This effectively screens the electron interactions beyond a certain distance (twice the ground plane spacing). This set-up allows a uniform electrostatic capacitance per unit length to be defined, using
the standard expression for capacitance of a wire above a ground plane (Burke 2002): -

\[ C_{BS} = \frac{2 \cdot \pi \cdot \varepsilon}{\cosh^{-1}(2L_g/r_{on})} \approx \frac{2 \cdot \pi \cdot \varepsilon}{\ln(L_g/r_{on})} \]  \hspace{1cm} (20)

Where \( L_g \) is the distance from the centre of the wire/nanotube to a parallel ground plane, i.e. the oxide thickness in Figure 3.6. In the same way, the quantum capacitances combine to reduce the potential energy with the addition of more modes. The kinetic inductances combine to reduce the kinetic energy so the kinetic inductances go in parallel (include a factor of \( \frac{1}{4} \) in the definition of \( L_{kin} \)).

A calculation of the Luttinger parameter, \( g \) for a specific experimental set-up is now possible. The number of modes in a SWNT is well defined, along with the oxide thickness. Typical theoretical estimates of \( g \) are in the range 0.2 – 0.3, so interactions are generally quite strong, given \( g = 1 \) is equivalent to a Fermi liquid.

In the case of a metallic tube, the non-interacting DOS, \( \nu_0 \) is constant at low energies (see Figure 3.4) so we would expect to see a simple power law, equation (19) reducing to (21). As long as the ‘tunnelling resistance’ or transmission coefficient of the tunnel barrier is not voltage dependent, which is a fair assumption for low voltages.

\[ \nu(E) \propto |E - E_F|^\alpha \]  \hspace{1cm} (21)

The energy can be supplied by temperature, \( k_B T \) or bias voltage. The power law exponent, \( \alpha \) is related to the Luttinger parameter \( g \) and the geometry of the tunnelling electrode as follows for a bulk contacted SWNT and end contacted SWNT: -

\[ \alpha_{end} = \frac{g^{-1} - 1}{4} \]  \hspace{1cm} (22)

\[ \alpha_{bulk} = \frac{g^{-1} + g - 2}{8} \]  \hspace{1cm} (23)

There is a greater suppression of tunnelling into the end of a LL than the bulk. Intuitively, this makes sense as tunnelling into the bulk allows the charge to spread away from the contact in two directions.
3.7.1 Power Law Observations in SWNTs

The power law predicted by equation (21), is readily observable from electrical measurements of SWNTs, as the differential conductance is always proportional to the tunnelling density of states (TDOS): -

\[
\frac{dI}{dV} \propto v(eV)
\]

(24)

This means that the power law can be observed from both zero bias conductance vs temperature and the differential conductance vs. voltage when \(eV > k_B T\): -

\[
G = \frac{I}{V} \propto T^{-\alpha} \text{ When } eV < k_B T
\]

(25)

\[
\frac{dI}{dV} \propto V^{-\alpha} \text{ When } eV > k_B T
\]

(26)

Bockrath et al (1999) observed these power law dependences together with the end and bulk contacting electrode geometry dependence, equations (22) and (23). Figure 3.22 shows the conductance temperature plots for both electrode geometries, and the spread of the exponents. The exponent value correlates strongly with the fabrication process order, end contacts being produced when the electrodes deposited on top of the SWNTs (\(\alpha \sim 0.35\)), and bulk contacts when the SWNTs were on top of the electrodes (\(\alpha \sim 0.6\)). The CB charging energy confirmed that the metal deposited on top of the SWNT electrically isolated the SWNT ends, and the island length was equal to the electrode separation. Equivalently, for contacts underneath the tube, the island length corresponded to the whole length of the tube.
Figure 3.22: Reproduced from Boekrath et al (1999). “Conductance $G$ plotted against temperature $T$ for individual nanotube ropes. The data are plotted on a log-log scale. a) Shows data for ropes that are deposited over pre-defined leads (bulk-contacted), whereas b) shows the data for ropes that are contacted by evaporating the leads on top of the ropes (end-contacted). Sketches depicting the measurement configuration are shown in the lower right insets. The plots show both the bare data (solid line) and the data corrected for the temperature dependence expected from the Coulomb blockade (CB) model (dashed line). We correct the data by dividing the measured $G(T)$ by the theoretically expected temperature dependence in the CB model. This correction factor only depends upon $[U = 2E_c] U/kaT$, and, since $U$ can be independently measured from the temperature dependence of the Coulomb oscillations, the correction procedure requires no adjustable parameters. If the CB were the only source of the temperature dependence, the dashed lines would be horizontal. Instead they have a finite slope, indicating an approximate power-law dependence on $T$. The upper left inset to 'a' shows the power-law exponents inferred for a variety of samples. Open circles denote end-contacted devices, while crosses denote bulk-contacted ones.”

Having taken precautions to prevent the substrate deforming the SWNT such deformations can be deliberately introduced in order to probe a variety of LL to LL
juncti on.

For junctions between Luttinger Liquids the following approximations apply:

- Bulk to bulk junctions: \( \alpha_{\text{bulk-bulk}} = 2\alpha_{\text{bulk}} \)
- End to bulk or visa-versa: \( \alpha_{\text{bulk-end}} = 3\alpha_{\text{bulk}} \)
- End to end: \( \alpha_{\text{end-end}} = 4\alpha_{\text{bulk}} \)

A number of such junctions have been reported. Highlighted here are those produced by Postma et al (2000) who created a 105° buckle in a tube (Figure 3.23a and b) and crossed two SWNTs (Figure 3.23c and d) using an AFM tip to manipulate the tubes. The conductance measurements showed power law behaviour, \( dI/dV \propto E^g \) (Figure 3.23e and f). Interpreting these results within LL theory gave consistent values of the Luttinger parameter, \( g = 0.26 \). The buckled tube was interpreted as end-to-end tunnelling, i.e. \( \alpha_{\text{end-end}} = 2\alpha_{\text{end}} \). The crossed tubes as, bulk-to-bulk tunnelling. Four terminal measurements were used, enabling the effect of the buckle to be isolated from that of power law contact conductance. This also enables \( g \) to be determined in a straight section. LL behaviour was observed up to room temperature. Naturally occurring tube junctions, assumed to be formed by a pentagon and heptagon defects, were observed by Yao et al (1999). The junction between two metallic tubes was found to show consistent power law behaviour as previously described with \( g = 0.22 \). Rectifying behaviour was observed in semiconducting to metallic tube junctions.
Figure 3.23: Reproduced from Postma et al (2000). a) AFM image before, b) after the creation of a 105° buckle in an initially straight SWNT with an AFM tip. c) Before, d) after the breaking of a SWNT and manipulating the ends back together, the ends extend ~100 nm beyond the crossing point. e) Differential conductance vs. bias voltage of a crossing sample, such as that pictured in ‘d’ at various temperatures. CB suppresses the conductance below 70 K. f) Differential conductance verses bias scaled by temperature, for a typical straight section and a nanotube manipulated into a crossing junction.

3.7.2 Other Evidence for a LL State in SWNTs

There are other mechanisms for producing a power law in an IV measurement, such as a non-conventional Coulomb blockade associated with a single tunnel junction rather than an island. However, such mechanisms cannot account for a power law when the DOS is probed without the removal of an electron. Ishii et al (2003) achieved just such a measurement using photoemission spectra to probe the DOS. The suppression they saw below 100 meV was observed in the binding energy vs. intensity, and, temperature vs. intensity. From this they extracted an exponent of $\alpha = 0.48$, which translated into the Luttinger parameter $g = 0.2$.

Position resolved STM, does involve the removal of an electron, but using such a tool on an individual SWNT provides evidence for a LL state beyond a suppression of the DOS as $V \rightarrow 0$. Using this technique Lee et al (2004) imaged the standing waves at the end of a SWNT. At the heart of the many pieces of evidence presented for a LL state in SWNT was the differing velocities of the spin and charge waves. The longer spatial wavelength of the charge mode was clearly visible, and the velocity could be extracted from the $E$-$k$ plot. Overall agreement with experiment and LL theory was very good, as the SWNT was on an Au substrate the interactions were considerably weaker with $g = 0.55$. 

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3.8 Power Law Predictions

In this section, the three most relevant theories for explaining the power law behaviour in MWNTs are introduced. This is in preparation for section 3.9 where the power law observations in MWNTs are featured together with the application of these theories. LL theory introduced in the previous section as an explanation for observations of a power law in SWNTs is extended to MWNTs. However, before that the two Coulomb blockade based theories are introduced.

3.8.1 Coulomb Blockade

Figure 3.24 shows two circuits, where an insulating material, thin enough so that electrons can tunnel through it, separates the conducting regions (grey). In Figure 3.24b the electrodes, source and drain are only separated by single tunnel barrier, or junction. Figure 3.24a appears to be more complicated with an island region separated from the electrodes by two tunnel junctions, although its behaviour is actually far simpler to explain.
Figure 3.24: Schematic of tunnel junctions. The circuit only shows the capacitance. The lead or tunnel junction resistance is not shown.

First we will consider the circuit behaviour without the effects of capacitance. This means the barriers are characterised only by their transparency to electrons, which is the probability of an electron tunnelling through the barrier. For low voltages this probability depends on the height and length (i.e. shape) of the barrier and is voltage independent. So the barrier is well described by a tunnelling resistance $R_T$. Consequently, both circuits in Figure 3.24 will behave ohmically, with resistances of $R_T$ for the single junction and $2R_T$ for the island case, assuming all the tunnel barriers are identical.

With tunnel junctions between the conducting parts, a current should flow based upon the transparency or resistance of the tunnel junctions. However, the junctions between the electrodes/island also have a capacitance, which means when an electron tunnels the charge on the junction capacitor or island is changed. The potential energy in a capacitor, $C$ is
Where \( Q \) is charge on the capacitor. If we add an electron we will alter the total charge, which is now \( Q + e \). The potential energy stored in the capacitor will increase. The change in the energy stored in capacitor is referred to as the \((\text{single electron})\) charging energy, \( E_C \): 

\[
E_C = \frac{e^2}{2C} \quad \text{(J)} \quad \text{or} \quad E_C = \frac{e}{2C} \quad \text{(eV)}
\]  

(28)

While \( C \) remains large, \( E_C \) remains insignificant, but when small enough capacitances are employed, \( E_C \) can be larger than the characteristic thermal energy of electrons, \( k_B T \). This will happen at room temperature for capacitances of around 3 aF, in this case a single electron cannot charge the capacitor without an additional supply of energy, e.g. from the bias voltage. A capacitance of 3 aF is very small so Coulomb blockade effects are often investigated at low temperatures, where larger capacitances can be used.

In this semi-classical picture, (Semi because we include the quantum mechanical effect of tunneling) after tunneling, the capacitor will charged to \( E_C \). This will always happen\(^1\), so the probability of this outcome is 1. This is shown graphically in Figure 3.25a, where the horizontal axis can be considered as the energy in the capacitor after a tunnelling event (the scale is normalised to the classical charging energy \( E_C \)). Figure 3.25a is plot of each of the possible outcomes against the probability of that outcome, and by ‘outcome’ we mean the energy in the capacitor after a tunnelling event. Figure 3.25a is not a plot of probability density, as this would simply be a delta function at \( E_C \), \( P(E) = \delta(E - E_C) \).

\(^{\text{1}}\) Successive tunnelling events are uncorrelated. An electron does not tunnel from the island to the drain at the same time as one enters the island from the source. Each tunnelling event changes the charge on the island.
Figure 3.25: Ideal Coulomb blockade. a) Probability b) normalised differential conductance vs. normalized bias voltage and c) normalised current voltage characteristic.

Once the bias has reached $eV/E_C \geq 1$, then tunnelling is no longer blocked, and current can flow based upon the barrier’s transmission properties. This can be seen in Figure 3.25c, which means at $E_C$ the differential conductance, $dI/dV$ goes from zero to one (Figure 3.25b). Integrating gives the $IV$ characteristic. The differential conductance is simply the integral of the probability density function, $P(E)$. 
In Figure 3.25b and c the actual barrier's transmission properties, described by a tunnelling resistance, $R_T$ have been normalised along with junction capacitance. The horizontal scale is shared with Figure 3.25a where the junction capacitance was also normalised. Having normalised out every parameter specific to a particular junction, Figure 3.25 has become a general description for every tunnel junction in the CB regime (i.e. $E_C > k_B T$).

The preceding explanation of the semi-classical picture of CB was very much geared towards the single junction case, although it also describes the $IV$ characteristics for both configurations in Figure 3.25. In the single junction case the capacitance, $C$ is the tunnel junction capacitance. In the island case the capacitance is the total capacitance of the island. In addition, in the island case the resistance to which the $IV$ would be normalised is the total resistance of the tunnel junctions in series.

The first observations of the Coulomb blockade were in an averaged form, resulting from granular metallic films. The first observations from a single island came from Fulton and Dolan (1987). In the island configuration a gate is often used so that the electrostatic potential on the island can be controlled or modulated.

The conventional, ‘conducting island’ form of CB is often observed in nanotubes, SWNTs and MWNTs, when the contacts meet the criteria for the tube being isolated or when disorder breaks up the tube into isolated sections. When the island is small enough to become a 0D object for electrons (length $< \text{mean free path}$), the quantisation of energy levels creates an additional potential energy requirement to the electrostatic capacitance, sometimes it is the greater energy requirement. The study of McEuen et al (1999) was featured earlier in section 3.3.2, where the role of disorder was discussed as a relevant example of CB.
Figure 3.26: Reproduced from McEuen et al (1999). a) Conductance vs gate voltage for a metallic SWNT, which forms a single island. b) Conductance vs gate voltage for a semiconducting SWNT, where several islands are formed creating a disordered CB charging spectra. The inset shows a greyscale plot of conductance (white = low G, insulating, black = high G, conducting) vs. bias and gate voltage.

As the temperature in Figure 3.26a is lowered, clear charging peaks emerge with the gate voltage. A peak corresponding to the number of electrons on the island changing. The same can be seen in Figure 3.26b, except the peaks are not orderly and the energy scales, (temperature and gate voltage) are much higher. This is because a number of smaller islands of differing size are in series. The disorder in the CB charging spectra is due to each island’s different charging energy, $E_C$ and the higher energy scale is the result of larger charging energies. The inset of Figure 3.26b is one of the classic representations of CB, a plot where the conductance is given by the contrast. Essentially it shows the same as Figure 3.25b, but with two voltage axes. For a single island a perfect diamond is seen, illustrating that the island becomes conducting when the gate voltage or bias is high enough or indeed combination of both. The disorder caused by the number of islands means the gate voltage on its own can never make the sequence of islands conducting (i.e. no dark lines cross the $V_{bias} = 0$ line), but a disordered diamond pattern is visible.

3.8.1.1 Single Junctions

Whilst it is possible to obtain an $IV$ characteristic quite closely resembling the ideal one in Figure 3.25c, for double junction systems this was not true for single junctions. A Coulomb offset was observed at high voltages, $eV \gg E_C$, but at low voltages the blockade appeared to be suppressed or weakened. To see why this happened we have to go beyond the semi classical picture, (where the only quantum mechanical effect is
the tunnelling of an electron), and treat the junction and its surrounding electromagnetic environment quantum mechanically.

![Figure 3.27: a) Tunnel junction, $C_J$ connected to the bias circuitry via $Z(\omega)$ which is the impedance of the leads in the junction vicinity ($\leq 1\mu m$). b) The equivalent circuit diagram. $C_{bias}$ is so much greater than $C_J$ (typically by a factor of $\sim 10^4$) that the single electron charging of $C_J$ does not significantly alter the voltage on $C_{bias}$, making the junction effectively voltage biased. (Note that $V \neq V_{bias}$ where $V$ is voltage across $C_J$).

A realistic model for the environment, $Z(\omega)$ in many cases is a transmission line, which is formed of distributed inductance, capacitance and sometimes resistance too. However, working with this model it can be difficult to see how the blockade is weakened. Following the approach in Flensberg et al (1992) and that of Ingold and Nazarov (1992) we first model the environment as a single inductor, $L$, which is a completely unrealistic case, but it will illustrate the effects of quantum mechanics on the single junction. Then, make the extension to a transmission line environment. The aim of this section is to show how the blockade is weakened, and not to provide a complete derivation of the theory, for this the reader is referred to Flensberg et al (1992) or Ingold and Nazarov (1992).

**Single Inductor Environment**

After an electron tunnels across the junction capacitor, $C_J$ discharges through the environmental impedance so that the voltage on the junction once more equals the bias voltage. If we set the bias in Figure 3.27 to zero and make $Z(\omega) = j\omega L$, Figure 3.28 becomes the equivalent circuit.
Figure 3.28: LC circuit, representing the junction and its environment.

If we suddenly move an electron from one side of the junction to the other, we will set the LC circuit ringing. Initially, all the energy will be potential energy stored in the capacitor \(e^2/2C_j\). The capacitor and the inductor will then continuously exchange this energy, oscillating at a rate determined by the circuit’s resonant frequency:

\[
\omega = \frac{1}{\sqrt{L \cdot C_j}}
\]  

(30)

The classical picture describes the oscillator having two distinct states, a ground state, where before the electron tunnels, the charge on the junction, \(q\) is zero and therefore the energy in the system will also be zero. In an excited state, immediately after a tunnelling event, \(q = e\), and the energy in the oscillator will be \(e^2/2C_j\) and all stored as potential energy. The quantum picture is different. The displacement of the oscillator and hence energy in the system is described by a probability distribution. But, if the energy in the oscillator were to be measured, it would be quantised in units of \(\hbar \omega\).

It's unlikely that the single electron charging energy \(E_C\) is divisible by an integer number of \(\hbar \omega\), so it is impossible for a electron to have tunnelled and left the oscillator with an amount of energy exactly equal to the classical charging energy \(E_C\). The electron can only leave the oscillator with a bit more or a bit less energy. At this point, it is convenient to introduce the parameter \(\lambda\). It is the number of \(\hbar \omega\) units that correspond to \(E_C\):

\[
\lambda = \frac{e^2}{2 \cdot C_j \cdot \hbar \cdot \omega} = \frac{e^2}{2 \cdot C_j \cdot \hbar \cdot \omega}
\]  

(31)

\(\lambda\) is unlikely to be an integer and it is not necessary. In the quantum picture \(\lambda\) corresponds to the average number of Bosons excited. When the quantised units of energy are small compared to \(E_C\), \(\lambda\) is large. The probability of leaving the oscillator with \(n\) Bosons is given by a Poisson distribution:
\[ P_n = \exp(-\lambda) \cdot \frac{\lambda^n}{n!} \] (32)

Figure 3.29 is exactly the same as is Figure 3.25a. Only this time with the quantum mechanical model there is more than one possible outcome for the energy in the capacitor after a tunnelling event. Figure 3.29 also shows the effect of the parameter \( \lambda \).

![Figure 3.29: Possible outcomes for the energy in the junction after a tunnelling event vs the probability of the outcome. Each line represents a possible outcome, on the normalised scale and they are separated by \( h \omega E_C \); for a) \( \lambda = 3.85 \), and, b) \( \lambda = 38.4 \).](image)

The link with the semi-classical approach can clearly be seen, as \( \lambda \to \infty \) the distribution will look like a delta function located at \( E_C \). Figure 3.29 is the key to understanding how the Coulomb blockade is broken, with current flowing when \( eV < E_C \), in both cases (Figure 3.29a and b). There are outcomes that have a significant probability which leaves the capacitor with less energy than \( E_C \). In fact, there is even a significant probability an electron can tunnel and leave the capacitor with zero \( h \omega \). In Figure 3.29a, this corresponds to a significant current as \( V \to 0 \). The corresponding differential conductance and IV characteristics are shown in Figure 3.30.
We have seen how the Coulomb blockade is broken when the system is treated quantum mechanically, and the importance of the parameter \( \lambda \), which controls the behaviour. In the quantum mechanical limit \( \lambda \to 0 \) and blockade is completely destroyed resulting in an ohmic \( IV \). In the classical limit \( \lambda \to \infty \), ideal offset ohmic behaviour will result, as the probability of an elastic tunnelling event, i.e. without exciting any Bosons becomes zero. This happens in the transmission line model, where all values of \( \omega \) are possible, and as \( \omega \to 0, \lambda \to \infty \) so an infinite number of low energy Bosons are excited. The elastic tunnelling seen for finite values of \( \lambda \) in the single inductor model becomes impossible. In the literature, this is referred to as the ‘orthogonal catastrophe’, simplistically meaning that elastic tunnelling is forbidden.
Next, it will be shown how $\lambda$ can also be expressed in terms of the quantum charge fluctuations on the junction capacitor.

The minimum energy in the classical description of a harmonic oscillator is zero, with the system at rest, $q(t) = 0$ for all $t$. In the quantum mechanical description, the system is never at rest, as this would violate the uncertainty principle. The charge $q$ (equivalent to displacement) is given by a probability distribution at the ground state, as it is in higher states too. Since the oscillator cannot be at rest the energy of the oscillator in its ground state cannot be zero. It is in fact $\frac{1}{2} \hbar \omega$, the energy spectrum of a harmonic oscillator is given by $E_n = (n+\frac{1}{2})\hbar \omega$ (where $n$ can be zero or a positive integer). The non-zero minimum energy is a direct consequence of the uncertainty principle.

Putting this energy into the $LC$ circuit gives the size of charge fluctuations. At one point in each cycle all the energy will be in the capacitor. At this point the current will be zero, the voltage at a maximum, and hence the charge $q$ will also be at its peak value, $q_{peak}$. Using the standard expression for the energy in a capacitor we get:

$$E = \frac{1}{2} \hbar \omega = \frac{q_{peak}^2}{2 \cdot C_j}$$  \hspace{1cm} (33)

The voltage and current in an $LC$ oscillator vary sinusoidally. Therefore, the charge will too, and so the peak charge, $q_{peak}$ and the root mean square charge are related as follows:

$$\sqrt{\langle q^2 \rangle} = \frac{q_{peak}}{\sqrt{2}}$$  \hspace{1cm} (34)

Rewriting equation (33) so that the charge is expressed in terms of the mean square charge:

$$\frac{1}{2} \hbar \omega = \frac{2 \langle q^2 \rangle}{2 \cdot C_j}$$  \hspace{1cm} (35)

Re-arranging yields:

$$C_j \cdot \hbar \cdot \omega = 2 \langle q^2 \rangle$$  \hspace{1cm} (36)
At this point, equation (36) can be inserted into equation (31), and λ the average number of Bosons excited is now expressed as the ratio of the charge displaced squared, $(\delta q)^2$, to the mean square charge fluctuations on the junction capacitor.

$$\lambda = \frac{e^2}{4\langle q^2 \rangle} = \frac{(\delta q)^2}{4\langle q^2 \rangle}$$

(37)

Finally, a couple of points to make before moving onto the transmission line model. As eluded to earlier, but stated specifically here on average the energy left in the capacitor/environment is the classical charging energy:

$$\frac{e^2}{2 \cdot C_j} = \hbar \cdot \omega = \sum_{n=0}^{\infty} \hbar \cdot n \cdot P_n$$

(38)

Also, the sum of all the probabilities is one, i.e. only one of the possible outcomes will happen.

$$\sum_{n=0}^{\infty} P_n = 1$$

(39)

These two statements are often referred to as the sum rules.

**Transmission Line Environment**

An LC transmission line is an extension of the simple LC circuit. In a semi infinite transmission line, it is possible for all frequencies or modes to exist rather than just one. In complete analogy with equation (36), the quantum charge fluctuations of the $k^{\text{th}}$ mode are:

$$\langle q_k^2 \rangle = C_{\text{line}} \cdot L_c \cdot \hbar \cdot \omega_k$$

(40)

The capacitance is the total capacitance, i.e. length of the transmission line, $L_c$ times the distributed line capacitance, $C_{\text{line}}$. The total energy is still $\hbar \omega_k$. The total charge displaced is obviously still $e$, but charge from each mode contributes to junction charge. The charged displaced in the $k^{\text{th}}$ mode by the addition of an election is $\delta q_k$ given by equation (41), which is arrived at from the solutions of the continuity equation and the equation of motion for the transmission line:
\[
\delta q_k = \frac{4}{\sqrt{1 + \left(\frac{C_j \cdot k}{C_{\text{line}}}\right)^2}} \tag{41}
\]

We are now in a position to define, \( \lambda_k \) the average number of Bosons excited in the \( k^{th} \) mode:

\[
\lambda_k = \frac{\langle \delta q_k^2 \rangle^2}{4\langle q_k^2 \rangle} = \frac{2 \cdot Z}{R_k} \frac{1}{1 + \omega_k \cdot \tau_d} \frac{1}{\omega_k} \left( \frac{2 \cdot \pi}{L_{\text{c}} \sqrt{\tau_{\text{line}}} \cdot C_{\text{line}}} \right) \tag{42}
\]

Where \( \tau_d \) is junction discharge time, i.e. \( \tau_d = C_j Z \).

Looking at equation (40), we can see that the size of the mean square charge fluctuations, \( \langle q_k^2 \rangle \) tends to infinity as the transmission line length, \( L_{\text{c}} \) does. Just as in the single mode case, large charge fluctuations equates to a small \( \lambda_k \rightarrow 0 \) (equation (42)). Therefore, the probability for exciting a particular mode goes to zero. But, if the sum of \( \lambda_k \) over all \( k \) values is taken, this goes to infinity, i.e. \( \sum_k \lambda_k \rightarrow \infty \).

This happens because \( \lambda_k \) diverges at the lower limit, i.e. as \( k \rightarrow 0 \). Physically, this represents the excitation of an infinite number of low energy modes. Despite being infinite in number, the energy in these modes is well behaved, agreeing with the sum rules of equation (38).

\[
\sum_k \hbar \cdot \omega_k \cdot \lambda_k = \frac{e^2}{2 \cdot C_j} \tag{43}
\]

The probability density function for a particular set of modes being excited by a tunnelling event is given by:

\[
A(\omega) = 2 \cdot \pi \cdot \sum_{\{m\}} \left[ \prod_k P_{n_k} \right] \delta \left( \omega - \sum_k n_k \cdot \omega_k \right) \tag{44}
\]

Energy is given in terms \( \omega \), \( \omega = eV/h \). The iterative product term is the probability for a particular set of excitations, equation (32) \((P_{n_1} \cdot P_{n_2} \cdot P_{n_3} ... \cdot P_{n_{\text{total}}})\), which weights the delta function located at the energy of the particular set of excitations. Finally, the probability density is the sum over all possible sets of excitations. However, getting from equation (44) to an \( IV \) curve is not as straightforward as in the single mode case, although the relationship is the same:
Equation (44) can be expressed in terms of \( a(\omega) \) which is the real part of the Fourier transform of the environmental impedance in parallel with the junction capacitor, i.e. Figure 3.28 where the inductor has been replaced with the transmission line impedance \( Z \).

\[
A(\omega) = \int_0^\infty dt \cdot \exp \left[ j \cdot \omega \cdot t \right] \exp \left[ E_c \cdot \frac{d}{2 \cdot \pi} \cdot a(v) \cdot \frac{\exp(-j \cdot v \cdot t) - 1}{h \cdot v} \right] \tag{46}
\]

The procedure for calculating the \( IV \) is to find the asymptotic form of \( A(\omega) \) as \( \omega \rightarrow 0 \), and then with some more algebra equation (46) can be written in a form which can be solved numerically, bearing in mind the transmission line equivalence of the sum rules, equation (38) and (39).

In the case of an \( LC \) transmission line the asymptotic form is:

\[
A(\omega) \propto \omega^{\frac{2Z}{R_k}} \tag{47}
\]

Therefore, a power law \( IV \) with an exponent of \( 2Z/R_k \) is observed when a single junction is connected to a transmission line:

\[
\frac{dI}{dV} \propto V^{\frac{2Z}{R_k}} \tag{48}
\]

As it is difficult to fabricate an electromagnetic transmission line with impedances that differ significantly from the impedance of free space, \( Z_0 \sim 377 \Omega \). The exponents in most experimental situations will be rather small, \( 2Z_0/R_k \sim 0.03 \), resulting in a somewhat washed out Coulomb blockade.

The impedance of a transmission line can be significantly increased with the addition of dissipation, at least in the frequency range where \( R' > \omega L_{D\text{line}} \). However, for an \( LCR \) transmission line, a power law is not found, and the asymptotic behaviour is given by (Flensburg et al 1992):

\[
A(\omega) \propto \exp \left[ - \frac{\omega_0}{\omega} \right] \tag{49}
\]
Where, $\alpha_b$ is constant proportional to $R'/C_{\text{line}}$. Therefore, although a strong zero bias anomaly is predicted with a resistive transmission line it is not characterised by a power law, nor could it easily be mistaken for a power law.

**Finite Traversal Time**

The key assumption in the theory above is the instantaneous tunnelling of the electron. Although very fast, the electron traversal time, $\tau_{\text{transit}}$, is in fact finite, $\sim 10^{-15}$s. What this means is that all transmission line modes that vary on the time scale of $\tau_{\text{transit}}$ or faster see the electron coming and are not suddenly displaced, they are adiabatically displaced. Hence modes, $\alpha_k > \tau_{\text{transit}}^{-1}$ are not shaken up, and therefore $A(\alpha)$ should not include these modes. Since these high-energy modes are no longer included, the average shake up energy, equation (43) is brought down, i.e. the classical charging energy is reduced.

An alternate manner in which to look at this, perhaps a more physical description, is to say these high energy modes move to their new state with unit probability, transferring charge down the transmission line. As the transmission line capacitance is charged, it is added (in parallel) to the junction capacitance. The transmission line capacitance is charged out to the horizon, a distance, $v\tau_{\text{transit}}$ where $v$ is the wave velocity on the transmission line, the addition capacitance is therefore $C_{\text{line}} v \tau_{\text{transit}}$.

### 3.8.2 Single Junction CB Observations

Once more Flensburg et al (1992) is an excellent source, comparing the observations of three single junction reports. Delsing et al (1989), Cleland et al (1990) and Gregory (1991) with EQF theory. There are other earlier reports of single junctions, but like Delsing et al (1989) and Cleland et al (1990) they may not have considered EQF as an explanation. As the theoretical papers, Devoret et al (1990) and Girvin et al (1990) appeared just one month and three months (respectively) after the publication of Cleland et al (1990). The later more detailed report of Cleland et al (1992) did include an application of EQF theory, which was found to produce a better agreement with the data than Cleland’s original model.

Delsing et al (1989) and Cleland et al (1990) used a conventional set-up of two lithographical defined Al strips, separated by an Al oxide to form the tunnel barrier. While, Gregory (1991) employed two crossed platinum wires for electrodes and an
adjustable barrier was created by a frozen helium film. The crossed wire set-up allows many slightly different junctions to be created, as the spacing between the wires is adjusted. But, unlike Al-oxide system, multi-junction arrays cannot be fabricated which is partly why much less is known about these systems.


In matching EQF theory to the experiments of Cleland et al (1990) and Gregory (1991), the low tunnelling resistance is a consistent problem, as “the present model [EQF] cannot accurately treat junctions with resistances close to the resistance quantum” - Flensberg et al (1992). For Cleland et al (1990) the tunnelling resistance, Rₜ ranges 29 kΩ - 8.8 kΩ, which straddles Rₓ ~ 25.8 kΩ. There are ways that the effects of a low tunnelling resistance can be included, although they are not fully developed, but when applied to the data of Cleland et al (1990) they do produce a better agreement with the data.

As a typical example of the agreement achieved between EQF and the experimental results, Figure 3.31 is reproduced from Flensberg et al (1992), showing how EQF reproduces the size and shape of the Coulomb blockade found by Gregory (1991) rather well. The theory takes noticeably longer to approach the asymptotic value (normalised dI/dV = 1), which Flensberg et al (1992) attributes to the subtraction of a quadratic background from the data.
Figure 3.31: Reproduced from Flensberg et al (1992), a comparison of EQF theory with the results of Gregory (1991). The symbols in the top panel are data from 5 different junctions and the lower panel shows EQF calculations for various values of capacitance, ranging 0.016 fF to 8 fF.

To conclude, the assessment of Flensberg et al (1992): “We find that the model agrees well with the size of the zero-bias anomalies measured for isolated single junctions. Quantitative comparisons between theory and experiment are complicated by the difficulty in independently measuring the details of the systems. However, based on the ability to fit most aspects of the experimental data with parameters consistent with the experimentally estimated parameters, we are confident that the present model correctly describes the effect of the electromagnetic environment in these systems.”

3.8.3 Egger and Gogolin (EG) Theory

Egger and Gogolin (2001) developed a model for tunnelling into a MWNT, treating it as a strongly interacting and disordered metal. Egger and Gogolin’s theory, referred to here as EG theory reproduces the key elements of the other theories (LL and EQF)
and those of the experimental observations (section 3.9), e.g. the power law behaviour, a Coulomb gap and $\alpha_{\text{ent}} \sim 2 \alpha_{\text{bulk}}$.

Instead of defining the environment in a phenomenological form, e.g. a transmission line it is defined macroscopically. The power law originates in a similar way as it does in EQF, from the spectrum of excited electromagnetic modes. EG theory does not generally produce an analytical expression for the exponent, so equation (50) comes with a few caveats.

$$\alpha_{\text{bulk}} = \frac{r_{\text{cut}}}{2 \cdot \pi \cdot \hbar \cdot D \cdot v_0} \cdot \ln(1 + v_0 \cdot U_0) \quad (50)$$

Where:

- $v_0$ is the non-interacting DOS. Given by:

$$v_0 = \frac{M}{2 \cdot \pi \cdot \hbar \cdot v_F} \quad (51)$$

- $U_0$ is the effective short ranged 1D interaction potential which is not necessarily the same as $U$ in section 3.8.4.

- $D$ is the diffusion constant, approximated by $D \sim v_F l$.

Commenting in their later paper, Egger and Gogolin (2002); “We wish to stress that the derivation of Equation (50) works only in the true 2D limit, characterized by a large number of bands $N$ or by $l \ll r_{\text{cut}}$”. Another important point is evident from Figure 3.32, which shows the numerical calculations for the TDOS. EG theory does not reproduce the power law in the limit $E \to 0$. The power law applies only above $E^*$, $E > E^*$.

$$E^* = \frac{D}{(2\pi r_{\text{cut}})^2} \quad (52)$$

Using the approximation $D \sim l v_F$, with a mean free path $l$, $0.5 \times 2 \pi r_{\text{cut}}$, $E^* \sim 6$ meV, for $l = 2\pi r_{\text{cut}}$, $E^* \sim 25$ meV. When $E > E^*$, charge diffusion is 2D and at low energies $E < E^*$, 1D behaviour takes over.

With Equation (50) so limited in its application, numerical methods are necessary to calculate the TDOS and eventually arrive at an exponent value. Figure 3.32 is a result of such a calculation.
Figure 3.32: Reproduced from Egger and Gogolin (2002). Normalised TDOS vs energy (analogous to Figure 3.30a). Egger and Gogolin use \( h = 1 \) and an energy scale set by \( v_F r_{cnt} \), for a MWNT with 7 nm radius this corresponds to 80 meV. Thus, the energy scale reads 0.08, 0.8, 8 and 80 meV. Insert is an Arrhenius plot of the same data.

The parameter set for calculation in Figure 3.32 is as follows:

- Mean free path, \( l = r_{cnt} \)
- Number of modes, \( N = 22 \).
- Interaction strength \( U_0 = 2\pi v_F \).

Using the same parameter set equation (50) predicts an exponent of \( \alpha = 0.23 \) which is much smaller than the observed exponent of \( \alpha = 1.97 \). In addition, the power law in Figure 3.32 extends to a lower energy range than that predicted by equation (52). This does indeed demonstrate that equation (50) really does only apply in the 2D limit.

The mean free path and the number of modes are quite tangible, but the meaning of an interaction strength of \( 2\pi v_F \) is far less tangible. This value actually corresponds to quite strong interactions, although \( U_0 \) is rather hard to define. Egger and Gogolin (2002) stating; "Unfortunately, it appears to be rather difficult to compute a realistic value for \( U_0 \)."
Changing only one parameter from Figure 3.32, resetting \( l = 10r_{cut} \sim 70 \) nm (referred to as the quasi ballistic case), which is far more in line with experimental observations gives an exponent of \( \alpha = 1.1 \). Still rather high but reducing the interaction strength such that \( U_0 = v_F \) gives \( \alpha = 0.3 \), in line with experimental observations.

The power law was a robust result of the numerical calculations, observed no matter what the ratio \( l/r_{cut} \). The exponent systematically decreased with reducing interaction strength and an increasing mean free path. Although not shown it appears EG theory is capable of generating large exponents; “We mention in passing that for suspended MWNTs or smaller doping levels, one may reach a regime of stronger interactions, where again power-law behaviour at intermediate energies is predicted, but with larger exponents.”

From Figure 3.32 it would seem the upper limit for power law behaviour, or rather when \( \tau(E)/\tau_0 = 1 \) is around 80 meV. Not shown here, the other result published in Egger and Gogolin (2002) with a smaller value of \( \alpha \), (1.1) showed the normalised TDOS \( \tau(E)/\tau_0 \) to achieve unity around 1 order of magnitude earlier, 8mV. Very little is made of the upper limit to the power law and the crossover to offset ohmic, one can only speculate whether the exponent is related to the upper limit of power law, i.e. higher exponent higher energy range of power law.

### 3.8.4 Luttinger Liquid in MWNTs

Egger (1999) describes how LL theory should be applied to MWNTs. The effect of the multiple shells is not to screen the e-e interactions; rather charge in the metallic bands of different shells is coupled (semiconducting bands were effectively ignored). This can be seen from how charge at one point on say the outermost shell will see charge some distance away, such as the screening length, e.g. 1 \( \mu \)m or so. To a donut shaped charge whose radius will be \( \sim 7 \) nm on the outer shell, another donut shaped charge a micron away will seem very much like a point charge, so if this donut shaped charge is also on the outer shell or on an inner one, the difference in terms of electrostatics is almost imperceptible a micron away.

Earlier in section 3.7 the strength of the interactions was characterised by the Luttinger parameter, \( g \). This is however dependant on the number of modes, \( N \). The
interaction potential or coupling constant \( U \) is the \( N \) independent component of the interaction strength, and is related to the Luttinger parameter as follows:

\[
g = \frac{1}{\sqrt{1 + N \cdot U}}
\]  

(53)

Given the exponent definitions, equations (23) and (22) the result is a rather slow transition of \( \alpha \sim N^{1/2} \) to a Fermi like behaviour where \( \alpha = 0 \). In fact equations (23) and (22) should really be re-defined as:

\[
\alpha_{\text{end}} = \frac{g^{-1} - 1}{N}
\]

(54)

\[
\alpha_{\text{bulk}} = \frac{g^{-1} + g - 2}{2 \cdot N}
\]

(55)

In applying LL to MWNTs there is essentially, little to add to section 3.7 where it was described for SWNTs. Similar exponents are often observed for MWNTs and SWNTs. This is difficult to explain within LL theory. A typical SWNT (or indeed MWNT) exponent is \( \alpha_{\text{bulk}} = 0.3 \) arising in a SWNT from a screening length of 250 nm. Taking a couple of MWNT scenarios, the same exponent requires a screening length of 20 \( \mu \)m for \( N = 20 \ (M = 5) \), or 4 \( \mu \)m for \( N = 16 \ (M = 4) \). Such screening lengths can arise for long MWNTs in freestanding geometries or an electrostatically equivalent geometry such as resting on an insulating glass substrate.

### 3.9 Power Law Observations in MWNTs

There are seven reports in this area and each one will be treated individually in chronological order. Naturally, each one has a different emphasis but there are three common elements.

- All of these measurements are the ‘on-substrate’ type
- The contacts are metals deposited onto the MWNT.
- They all treat LL theory as a potential explanation for the data.

#### 3.9.1 Schönenberger et al (1999)

Schönenberger et al (1999) conducted a detailed study which employed many techniques in an attempt to establish the conduction mechanisms in MWNTs, that.
were dispersed onto SiO₂ and subsequently contacted by evaporated gold electrodes, Figure 3.33a. An additional aim was to reconcile this data to reports of ballistic conduction of the deHeer group, e.g. Frank et al (1998) and later Poncharal et al (2002).

Schönenberger et al (1999) interpreted many of the experimental results within a WL picture, (1D or 2D - diffusive conduction) whilst acknowledging, “that the theories are rigorously speaking no longer valid”. With various values for the free path extracted Schönenberger et al (1999) concluded; “all our results can therefore be consistent only if \( l_i \) is of the order of the circumference; not very much larger, but also not very much smaller”. However, the contradictions between the data that was interpreted within traditional FL theories is only part of the problem. The zero bias anomaly characterized by a power law (Figure 3.33b) could only be tentatively interpreted within LL theory. The exponent of \( \alpha = 0.36 \) is comparable to that found in SWNTs and was therefore interpreted as arising from a bulk contact to a single shell.

Figure 3.33: A reproduced from Schönenberger et al (1999). a) SEM image of MWNT on SiO₂ contacted by 4 Au fingers. b) Differential conductance – bias voltage for various temperature, the grey dotted line is the power law \( dI/dV \sim V^{0.36} \), inset zero bias conductance verses temperature on log – log scale where the power law appears a straight line.

Other points to note is that the power law is on a rather low energy scale. The measurement was asymmetric beyond 20 mV, and the contact resistances are low \( (<<R_k) \) and as acknowledged in Schönenberger et al (1999) the \( dI/dV - V \) data fit is not perfect.
3.9.2 Graugnard et al (2001)

Graugnard et al (2001) performed two terminal measurements of single MWNTs and small ropes, although only one MWNT in the rope formed a bridge between the contacts. The selection technique opens both ends of the MWNTs, so uniquely among the power law papers reviewed all layers in the MWNT should be contacted at both ends.

At room temperature, the two terminal conductance typically varies between 0.2 and 2.8 $G_0$, although a conductance as high as 27 $G_0$ was recorded. If only the outer shell were contacted, these kinds of conductance values would correspond to almost completely transparent contacts, i.e. a 2$G_0$ conductance. Considering only the metallic shells, which would number approximately 5, the typical room temperature conductance per shell would be around $\sim 0.2 \, G_0$ (65k$\Omega$).

Upon cooling the ohmic behaviour gives way to a conductance gap below 20K. The conductance gap or zero bias anomaly (ZBA) can be characterized by an energy dependant power law, with exponents, $\alpha$ between 0.17 and 0.43 (established by $G$-$T$ and $IV$ data).

However, the data fits are not as good as they could be (Figure 3.34b). Graugnard et al (2001) argues that this is because of the low resistance of the tunnelling contacts relative to the intrinsic nanotube resistance i.e. the voltage division factor, $\eta$ is smaller than 0.5. $\eta$ would normally be $\sim 0.5$ for a tube connected at either end via two identical, high resistance tunnelling contacts.
Figure 3.34: Reproduced from Graugnard et al (2001). “A plot of $G(V,T)$ vs. voltage at six temperatures”. “The data is shown as symbols, and the theoretically calculated curves are shown as dashed lines”. a) Corrected data fits for fixed $\eta$. b) Uncorrected data fits.

Using a least squares procedure the MWNT conductance was determined from the low temperature data. It assumed that the MWNT conductance is constant. $\eta$ will, of course, change with temperature and voltage, even if the MWNT conductance is constant. But, the simple procedure where the same value of $\eta$ is used throughout gives much better data fits (Figure 3.34a). Although the data fits themselves change to something just off a power law. A further refinement was made, to determining $\eta$ self consistently at every temperature and voltage; this improved the fits still further. Typically $\eta$ was found to be as low as $\sim 0.1$. A voltage drop along the MWNT was observed using Kelvin force microscopy (KFM), validating the approach of including a nanotube resistance.

With the improved data fits, the exponent values are shown in Table 3.1 below along with the Luttinger parameter, $g$ which was extracted from the exponent. Graugnard et al (2001) was not certain if the exponent should be interpreted as originating from a bulk or end contact. The bold highlighted values indicate which one is likely to be the correct interpretation given the reported values of $g$. 
Table 3.1: From Graugnard et al (2001). Exponent and the corresponding Luttinger parameter for a bulk or end contact interpretation. *not enough low temperature data to obtain a reliable fit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exponent, (\alpha)</th>
<th>(g(\alpha_{\text{bulk}}))</th>
<th>(g(\alpha_{\text{end}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25(^a)</td>
<td>0.94</td>
<td>0.11</td>
<td>0.21</td>
</tr>
<tr>
<td>29</td>
<td>0.56</td>
<td>0.16</td>
<td>0.31</td>
</tr>
<tr>
<td>34</td>
<td>0.53</td>
<td>0.16</td>
<td>0.32</td>
</tr>
<tr>
<td>41</td>
<td>0.58</td>
<td>0.15</td>
<td>0.30</td>
</tr>
<tr>
<td>66</td>
<td>0.39</td>
<td>0.20</td>
<td>0.39</td>
</tr>
<tr>
<td>87</td>
<td>0.36</td>
<td>0.21</td>
<td>0.41</td>
</tr>
</tbody>
</table>

There is of course a conceptual problem applying LL theory in MWNT and considering only one shell, \(M = 1\). An electron suddenly entering a LL (i.e. through a tunnel barrier) excites an infinite number of plasmons, and the excitations will be coupled to all conducting shells in the MWNT (section 3.8.4, Egger (1999)). In addition, the comparison with the Luttinger parameter, \(g\) found in SWNT experiments with different geometries is a bit misleading; \(g\) is \(M\) (shells) or \(N\) (modes) dependant.

Graugnard et al (2001) conducted the measurements on a glass substrate, with electrode separation of \(\sim 4\) \(\mu m\), so with no conducting back gate to screen the interactions beyond a few hundred nm, the interaction should be stronger. Using 4 \(\mu m\) as the screening length, and the interaction potential definition from Bockrath (1999). Exponents have been calculated based on a more realistic number of participating shells are shown in Table 3.2. This time the bold italics correspond to the scenarios which produce exponents in the range of those found by Graugnard et al (2001). Although the lowest exponent observed, 0.36 seems to fall between scenarios, the fit with exponents found by Graugnard et al (2001) is very good.
<table>
<thead>
<tr>
<th>Participating shells, $M$</th>
<th>$g$</th>
<th>$\alpha_{\text{end}}$</th>
<th>$\alpha_{\text{bulk}}$</th>
<th>$\alpha_{\text{end-end}} = 2\alpha_{\text{end}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.09</td>
<td>0.65</td>
<td>0.30</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>0.59</td>
<td>0.27</td>
<td>1.18</td>
</tr>
<tr>
<td>6</td>
<td>0.07</td>
<td>0.54</td>
<td>0.25</td>
<td>1.08</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>0.50</td>
<td>0.24</td>
<td>1.01</td>
</tr>
<tr>
<td>8</td>
<td>0.06</td>
<td>0.47</td>
<td>0.22</td>
<td>0.95</td>
</tr>
<tr>
<td>9</td>
<td>0.06</td>
<td>0.45</td>
<td>0.21</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Table 3.2: Calculated exponent and $g$ values for a range of participating shells and the electrostatic geometry in Graugnard et al (2001).

Although it works very well in practice, there is a conceptual problem when adding in a voltage drop along the nanotube; LL theory applies for a ballistic conductor and there should be no voltage drop in the bulk. Postma et al (2000) is referenced for a precedent on low $\eta$ values. However, the situation in this paper is different. It is SWNT manipulated to create end-end or bulk-bulk junctions, therefore there are three voltage drops compared to normal two; 1) contact-NT, 2) NT-NT and 3) NT-contact. There is no voltage drop in the bulk.

Another uncertainty is if the connections to the MWNTs in these experiments meet the criteria for a tunnel junction, which forces a sudden entrance of an electron into the LL. The room temperature two terminal resistances are certainly on the borderline or even the low side in terms of what is required for CB, i.e. $R_T > R_K$ (25 kΩ), where the 'sudden' entry of an electron is also a criteria.

It is also worth noting that Graugnard et al (2001) excluded the following conduction mechanisms:

- Thermally activated conduction
- Simple two-band model appropriate for graphite
- A zero in the transmission probability induced by gap states
- Variable range hopping mechanisms
- 1D and 2D weak localization

3.9.3 Bachtold et al (2001)

The fabrication procedure employed in Bachtold et al (2001), (evaporating gold contacts on top of a MWNT) typically produces low resistance contacts (~1 kΩ) but occasionally higher contact resistances are produced (>10 kΩ). One of the featured MWNTs was contacted by three electrodes, one of which had a contact resistance of 140 kΩ. In many respects this is an ideal experimental setup, a MWNT contacted with just one tunnel barrier.

A parallel magnetic field was applied ranging 0-15 T, the $dI/dV - V$ characteristics showed a pronounced dip at $V \rightarrow 0$ which was unaffected by magnetic field strength. However, the $dI/dV - V$ structure at voltage ranges beyond the dip showed peaks whose position was affected by the magnetic field. The data was interpreted within the Aharonov-Bohm effect. The peaks where assigned to broadened Van-Hove singularities, there spacing was in agreement with the expected sub-band spacing for a MWNT. The Van-Hove singularities are broadened due to scattering from disorder; this demonstrates that the elastic length is of the order of the circumference, $l_e \sim 2 \pi r_{cnt}$. Therefore, the MWNTs are not in 2D diffusive regime.

Returning to the conductance dip at $V \rightarrow 0$, Figure 3.35 shows how an energy dependant power law characterises this dip. Figure 3.35a shows the evolution of the conductance dip with decreasing temperature (0.35 K - 20 K), the same format as Figure 3.34 from Graugnard et al (2001). Figure 3.35b is log-log plot of conductance vs temperature, $G(V = 0, T)$. The straight line clearly indicating a power law with the gradient giving an exponent, $\alpha = 0.36$. Finally, Figure 3.35c shows the equivalence of voltage and temperature as energy sources. Measurements made at various voltages and temperatures collapse onto a universal scaling law.
Figure 3.35: Reproduced from Bachtold et al (2001). a) $G(V, T = \text{const}) = dI/dV$ for $T = 0.35-20\text{K}$. b) The linear conductance $G(0,T)$ on log-log scale showing power law. c) $G(V,T)T^\alpha$ vs $eV/k_BT$. for $eV \gg k_BT$ $G \sim V^\alpha$.

Using AFM manipulation different junction configurations were fabricated to test if the exponent behaved in the same way as it had in the experiments with SWNTs e.g. Postma et al (2000). Namely:

- $\alpha_{\text{end}} \sim 2\alpha_{\text{bulk}}$
- $\alpha_{\text{end-bulk}} \sim 3\alpha_{\text{bulk}}$
- $\alpha_{\text{end-end}} \sim 2\alpha_{\text{end}}$

Figure 3.36a and b shows the MWNT configurations and the exponents extracted from the $GV$ characteristics are shown in Figure 3.36c. The exponents do indeed scale as predicted by LL theory for different junction configurations.
Figure 3.36: Reproduced from Bachtold et al (2001). AFM images of MWNTs junctions created by AFM manipulation. a) Arrow indicating location of end-bulk junction. b) Arrow indicates end-end junction. c) “G as a function of V in a double logarithmic plot for a Au-bulk, an end-bulk, and an end-end junction. The corresponding slopes are $\alpha = 0.25, 0.9, \text{ and } 1.24$, respectively.”

The analysis focuses on three possible explanations:

1. Luttinger Liquid, (LL) large $N$.
2. Environmental Quantum Fluctuations, (EQF) large $N$.
3. Egger and Gogolin’s disordered MWNT CB theory.

The first two are treated as indistinguishable as for the case of large $N$, the predicted exponents for the various geometries are identical. Bachtold et al (2001) assumes a line capacitance of 30 aF/μm (the oxide thickness was not stated but this corresponds to an oxide 20 nm thick), its also stated that $N = 10-20$, as a result of the hole doping of MWNTs. Alternatively the origin of the many modes could be the participation of inner metallic shells. $N = 10-20$ corresponds to 3-5 participating metallic shells, an example inductance of 1 nH/μm is given ($N = 16, M = 4$). With these parameters the line impedance is 5.7 kΩ, equating to $\alpha_{\text{end}} = 0.44$ or $\alpha_{\text{bulk}} = 0.22$. This is a little lower than the experimental value of $\alpha_{\text{bulk}} = 0.36$ but compares fairly well. However, if all metallic shells are participating $M = 4$ ($N = 16$) is reasonable, but lower than the average value for the number of metallic shells.

The MWNT could be considered a disordered conductor; perhaps an RCL transmission line would be a more accurate way of view the impedance in EQF theory. Not all the contacts are tunnelling contacts so an upper limit on the resistance of these MWNT can be accurately established; if the resistive component is
\( R' \sim 5 \, \text{k}\Omega/\mu\text{m} \) then the inductive part of the transmission line, \( \omega L \) is equal to the resistive part for \( h\omega = 3 \, \text{meV} \). As a power law is observed for much higher voltages than 3 mV, the resistive part can be neglected.

The exponent found for EG theory can be expressed in terms of measurable parameters:

\[
\alpha_{\text{bulk}} = \frac{20 \cdot r_{\text{cei}}}{N \cdot l_e} = \frac{20 \cdot r_{\text{cei}} \cdot R'}{R_e} \tag{56}
\]

Bachtold et al (2001) calculates the bulk exponent predicted by EG's theory to be 0.02 to 0.08. Assuming \( N = 16 \) as before, these results have corresponding elastic mean free paths of \( l_e \sim 440 \, \text{nm} \) (~10 × circumference, \( R' \sim 3.6 \, \text{k}\Omega/\mu\text{m} \)) and \( l_e \sim 80 \, \text{nm} \) (~2.5 × circumference, \( R' \sim 14.7 \, \text{k}\Omega/\mu\text{m} \)). With these parameters the total elastic mean free path would have to be just over half the circumference, \( l_e = 24 \, \text{nm} = 0.55 \times \) circumference (\( R' \sim 66.7 \, \text{k}\Omega/\mu\text{m} \)). In order for EG theory to predict exponents found experimentally, \( l_e \) must be unrealistically small given we know \( l_e \) to be greater than the circumference as Van-Hove singularities are present (1D signatures) and the measured tube resistance, is well below that which corresponds to the rather low value of \( l_e \) needed.

Summarising, Bachtold et al (2001) demonstrates the geometrical dependence of the power behaviour in MWNTs, typical bulk exponents, \( \alpha \sim 0.36 \). Although perhaps the exponents are a little large, the results are in good agreement with a large \( N \), LL or EQF theories. EG theory could not explain the exponent values; it required elastic mean free paths well outside those determined experimentally.

### 3.9.4 Tarkiainen et al (2001)

In terms of exponent values, Tarkiainen et al (2001) offers only slightly different exponent values, \( \alpha = 0.12 - 0.32 \). This is not surprising as the experiment is essentially the same; two evaporated gold contacts onto which MWNTs are placed, although in one sample the MWNT is resting on the SiO\(_2\) beneath the gold contacts. What is new is observation of the Coulomb offset, the previous reports did not show this.

Fits to the Coulomb offset give a tunnelling resistance \( R_T \sim 20 - 68 \, \text{k}\Omega \), and \( C_T \) the total capacitance 31-111 aF, which corresponds to charging energies of 2.5 - 0.7 meV.
The charging energies are indeed very low. Looking back to the results of Bachtold et al (2001) the power law was observed to at least 100 mV (Figure 3.36c), with the tube lengths and electrodes being similar. The tunnelling resistances are on the right side of the minimum tunnelling resistance to observe CB, \( R > R_K \) (25.8 kΩ)

The capacitance extracted from the measurements, \( C_T \) is assumed to originate from the total MWNT capacitance for half of its length, this gives \( C_{\text{line}} \sim 70 \text{ aF/μm} \). This is a rather high capacitance corresponding to a MWNT just 6 nm away from a ground plane. But then, a significant portion of the MWNT is on top of the metal electrodes which would produce a much larger electrostatic capacitances.

\[
C_{\text{line}} = \frac{2 \cdot C_T}{\text{length}}
\]  

(57)

With values for the line capacitance, \( C_{\text{line}} \) and the exponent, the kinetic inductance can then be calculated for both an EQF and a LL interpretation. The median value found was 0.5 nH/μm, when compared to theoretical predictions (equation (9) multiplied with a factor of \( N^3 \)) corresponds to 8 shells participating, assuming 1/3 layers are metallic this corresponds to 24 shells in total. The variation in values for the kinetic inductance is probably due to the variation in the number of metallic shells. Additionally, the kinetic inductance values found for an EQF interpretation showed a broader scatter than those for LL interpretation. This leaves Tarkiainen et al (2001) to conclude that EQF is better suited at high voltages, but no distinction can be made at lower voltages.

There is an issue arising from the way the line capacitance has been defined to arise from an averaged line capacitance of the nanotube. The value itself is fine, and it can be replicated by assuming MWNT overlapping the contact has a separation to the ground plane of 0.7 nm and the distance to the ground plane between contacts it is around 200nm. The issue is to say the exponent arises from impedance defined from an average line capacitance, which is an average that includes a contribution from that over the contacts. This is not how it was applied by Bachtold et al (2001). Taking \( C_{\text{line}} \) to be the line capacitance between the electrodes is how one arrives at the prediction for a large-\( N \) LL and a large-\( N \) quantum wire in EQF to predict the same exponents, e.g. Bockrath (1999). Tarkiainen et al (2001) includes no justification for equation (57), other than the capacitance is to be split between the junctions at each contact.
The fact is, without including contributions to the capacitance from the MWNT-contact overlap the extracted line capacitances would just be too high, i.e. imply the ground plane was impossibly close. What Tarkiainen et al (2001) has done makes the analysis work, however with only four samples it is difficult to establish a correlation of any sort between the extracted capacitance and the various length parameters, i.e. total, contact-overlap and between contacts length. This kind of correlation could justify a particular approach in defining the capacitance used for interpretation of the exponent.


Although Liu et al (2003) reports in Boron doped MWNTs it is worth briefly covering this study as power law behaviour was observed. A power law decrease in conductance is observed at low temperatures (< 30 - 50 K). At higher temperatures 50 – 300 K, the conductance increases slightly, (3%) with decreasing temperature. As expected for metal in which the resistance decreases because electron-phonon scattering decreases at low temperatures. The increase in the resistance can be fitted by a power law with a very small exponent, $\alpha \sim 0.02 - 0.05$, Figure 3.37.

![Figure 3.37: Reproduced from Liu et al (2003). Conductance temperature on a log-log scale.](image)

Liu et al (2003) points out that for LL based theory to explain these exponent values, they would have to have 15 metallic shells (~45 shells in total), which is not realistic for these MWNTs or indeed for arc discharged produced MWNTs in general. Instead, the low temperature increase in resistance is explained with WL theory; in this low
temperature regime negative magnetoresistance was observed. All of the observations could be explained with 1D WL, \( l_p \sim 200 \text{ nm} \) at 70 K. Given that a substitutional boron atom is expected approximately every 10 nm, Liu et al (2003) concluded that the large diameter of MWNTs does indeed enable them to tolerate point defects, thanks to the averaging of disorder around the circumference (White and Nodorov, 1998).

### 3.9.6 Kanda et al (2004)

Despite reporting similar exponent values, \( \alpha = 0.05 - 0.35 \) Kanda et al (2004) showed a completely new aspect of the power law found in MWNTs. This was that the exponent, \( \alpha \) can be significantly affected by the gate voltage and perpendicular magnetic fields (Bachtold et al (2001) only applied a parallel B field which had no effect on the power law). The samples are fabricated in a similar way to those previously, i.e. metal evaporated onto MWNTs dispersed onto a Si/SiO\(_2\) wafer. However, the choice of Vanadium as the contact metal is unusual, perhaps due to poor sputtering conditions it proved not to be superconducting, at least down to 4K. There is also common ground with Graugnard et al (2001), where the room temperature two terminal resistances were quite low 8.5 - 14 k\( \Omega \).

Kanda et al (2004) focused on two MWNTs, but before these results are shown it is worth noting that not all the MWNTs studied showed power law behaviour. Some showed conductance decreasing faster than a power law. Figure 3.38 shows the main results, the zero bias conductance versus temperature is well fitted by a power law and the exponents were found to be the same from the differential conductance plots (not reproduced here). Figure 3.38b shows an inflection point, \( T^* \) at which the exponent changes from 0.33 to 0.15. The higher temperature exponent is always lower than the low temperature exponent. Figure 3.38c and d shows how the exponent oscillates with gate voltage for two different samples.
Figure 3.38: Reproduced from Kanda et al (2004). a) Zero bias conductance verses temperature at two different gate voltages. b) Inflection point in the zero bias conductance – temperature data. c and d) Gate voltage dependence of exponent for two samples. The arrows indicate where there is an inflection point such as that shown in (b).

Kanda et al (2004) considers two theories with which to explain the data; LL and EG theory. LL can be dismissed on the basis that the exponent oscillates smoothly with gate voltage rather than peaking at a single point close to gate voltage = 0 with staircase slopes on each side. Additionally, the gate voltage required to change the number of modes at $E_F$ can be readily calculated, and Kanda et al (2004) finds this to be of the order of 100V, where as the exponent changes on a scale of about 1V. Therefore, LL fails to explain the results qualitatively and quantitatively.

Kanda et al (2004) turns to EG’s theory to explain the results. In EG’s theory the number of modes and the interaction strength influence the exponent as in LL theory, but crucially so does the level of disorder, i.e. the mean free path. It has been shown theoretically that the influence of an individual defect within a nanotube changes with the Fermi level (i.e. the gate voltage) and this has been experimentally confirmed by Bockrath et al (2001). It is therefore quite possible that more than a few defects could cause the mean free path to vary in a complicated manner with gate voltage.

The exponent for EG theory is expressed by Kanda et al (2004) as:

$$\alpha_{\text{bulk}} = \frac{r_{\text{ex}}}{l \cdot M}$$

(58)
This is equivalent to the expression given by Bachtold et al (2001), equation (56). However, Kanda et al (2004) considers the number of modes to be less, $N \sim 10$ ($M \sim 2.5$) and the mean free path to be less than the circumference, $l \leq 2\pi r_{\text{cm}}$. Stating $l \sim 5-60 \text{ nm}$, this gives a range of exponent values 0.01 - 0.16. While the exponents that are calculated using the parameters given by Kanda et al (2004) overlap the experimentally observed values in the range 0.05-0.16, the higher exponent, values up to 0.36 are not explained with this calculation, leaving Kanda et al (2004) to conclude that equation (58) produces exponents "near the experimentally observed values".

The inflection temperatures, after which lower exponents are observed (Figure 3.38b) are assigned a "possible cause" as a sign of the limited energy range over which a power law can be expected in EG theory. The temperature range of the $T^*$ values is cited as supporting evidence for the interpretation. However beyond the power law regime EG theory predicts $\alpha = 0$ (i.e. offset ohmic behaviour). Kanda et al (2004) does not report this, and suggests further theoretical and experimental work.

Kanda et al (2004) also found a perpendicular magnetic field (up to 4 T) usually reduced the exponent, suggesting the exponent value could be influenced via the diffusion constant, $D$ ($D \sim N_{\text{eff}}$). This was referenced to the theoretical work of Roche and Satio (2001), who found magneto resistance of a large diameter nanotube in a perpendicular magnetic field could be negative (for $l_e < 2\pi r_{\text{cm}}$) or positive (for $l_e > 2\pi r_{\text{cm}}$) depending on the disorder level, and that the strength of the effect was effected by the position of the Fermi level. The effect of a B field on the exponent is a convergence of two (magneto resistance in MWNTs and the power law, zero bias anomaly in MWNTs). The origins of both these phenomena are still very much the subject of debate.

In summary, Kanda et al (2004) have shown how exponent, $\alpha$ can oscillate with gate voltage. A behaviour which cannot be explained with LL theory. Instead the results are explained within the framework of EG's non-conventional Coulomb blockade theory which successfully explains the main features.

**3.9.7 Kanbara et al (2004)**

Shortly after Kanda et al (2004), Kanbara et al (2004) also reported power law behaviour in MWNTs with a gate voltage dependence. It is a conventional setup of
Pt/Au electrodes evaporated onto MWNTs dispersed onto a degenerately doped Si wafer with 200 nm oxide. The exponents are determined from the conductance - temperature characteristics, which followed power law dependence for the whole of the data range presented 20-300 K. no IV data for the MWNT itself is presented. Figure 3.39 shows the main result from Kanabara et al (2001), an exponent, $\alpha$ dependant on the gate voltage, $V_G$, peaking around $V_G = 0$ V.

Figure 3.39: Reproduced from Kanabara et al (2001). Exponent found from G-T measurements verses gate voltage, $V_G$.

In terms of an LL interpretation, Kanabara et al (2001) states that large exponents are expected for end contacted SWNTs (0.94) and much lower values are expected for a 10 shelled MWNTs (0.29). So Kanabara et al (2001) concludes with a peak exponent of $\alpha = 0.64$ that an end contact has been formed and the outer shell dominates. Also, stating the exponents found by Egger and Gogolin (2002) range 0.23 - 2.0 so LL and EG's theory cannot be distinguished.

Figure 3.39 is indeed qualitatively how one would expect the exponent to behave if the gate modified the exponent via the number of modes participating. Based on the
numbers\(^2\) given in Kanbara \textit{et al} (2001), a scenario of two metallic shells participating at \(V_G = 0\) gives an end exponent of \(\alpha_{\text{end}} = 0.69\), which accounts for the peak value. LL theory predicts a rather slow crossover for the exponent, as \(N \to \infty\), \(\alpha \to 0\) but as \(N^{1/2}\), indeed \(\alpha_{\text{end}} = 0.1\) corresponds to \(N = 100\), this is roughly in agreement with gate coupling and Figure 3.39 of Kanbara \textit{et al} (2001). Applying EG’s theory as in Bachtold \textit{et al} (2001) the peak value can be accounted for as an end exponent with \(N = 4\) and a mean free path 2-3 times the circumference. However, the exponent is inversely proportional to the number of modes and based upon the gate coupling in Kanbara \textit{et al} (2001), it should decrease much faster than shown in Figure 3.39.

There is however a problem with the LL interpretation, both versions. The number of participating sub-bands (and hence modes) is increased due to participation of semiconducting sub-bands, for the LL picture these are considered ballistic. This is not reasonable, especially over the 1.5\(\mu\)m that separate the electrodes, the most favorable comparison would be with the work of Poncharal \textit{et al} (2002) where the mean free path in the semiconducting sub-bands was extracted as 200 \(\text{nm}\).

\textbf{3.9.8 Discussion}

Lets summarise some of the facts surrounding the issues for discussion such as:

- The exponent values.
- The energy range of the power law.
- The tunnelling resistances.

The maximum exponent seen for a metal to MWNT junction in most reports is around 0.36, Kanbara \textit{et al} (2004) being a bit of an exception at 0.64. The minimum exponents have a much wider spread, either ~ 0.2 or much lower indeed, close to zero.

The energy range of the power law measurements presented is often quite small, the gate voltage papers range to the highest temperatures. Kanbara \textit{et al} (2004) is the only one to show \(GT\) characteristics to 300 K and measurements in Kanda \textit{et al} (2004) go

\(^2\) The first semiconducting sub-band being reached at \(V_G = 0.5\ \text{V}\), the slightly smaller than average diameters of 4 - 10 \(\text{nm}\) and the oxide thickness of 200 \(\text{nm}\).
to 200 K. In terms of voltage range there is a wide variation. Tarkianen et al (2001) and Schönenberger et al (1999) showed a power law to only ~5 mV and 20 mV respectively, while the other reports range up to 50 – 100 mV.

The apparent tunnelling or contact resistances vary widely amongst the reports. They can be categorized relative to the quantum resistance, \( R_K \sim 26 \text{ k}\Omega \), as low, medium or high, i.e. < \( R_K \), ~ \( R_K \) and \( R_K \) > respectively. Three reports have rather low resistances while the remaining can be described as medium-high or high.

### 3.9.8.1 Exponent Values

With typical exponents around 0.36, the similarity with SWNT experiments such as Bockrath et al (1999) is striking. Given this, it is very tempting to assume exactly the same physics is responsible for both observations. With varying degrees of certitude this was what Kanbara et al (2001), Graugnard et al (2001) and Schönenberger et al (1999) all proposed. It is however incorrect to apply LL theory to a MWNT in this way. The excitations within a LL as an electron enters would couple to all the conducting modes in a MWNT (Egger 1999). The case with the smallest number of modes, \( N \) is that of all metallic shells participating, i.e. \( N = \frac{1}{2} \times 4 \times \text{number of shells} \).

With this in mind, whether LL remains a possible explanation for the power law, depends very much on the electrostatic geometry, i.e. can strong interactions counter balance the effect on \( \alpha \) of introducing many modes? This was the case for Graugnard et al (2001), where no ground plane was present and LL theory reproduced exponents comparable to experimental results.

Large-\( N \) LL and EQF are the same in terms of exponent value. So where one works, so should the other. In some circumstances, however, the case for both is not equally strong. For example in Kanbara et al (2004), the modes brought into the LL as \( V_0 \) increases are required to be ballistic in the LL interpretation. However, in an equivalent EQF interpretation, it has to be justifiable to model them as an \( LC \) transmission line. There is a subtle difference; following the line of reasoning in Bachtold et al (2001) any resistive portion element can be neglected if it is insignificant when compared to the inductive part. For MWNTs resistances typically reported, this happens at very small energies, ~ 3 meV. Thus, for an EQF
interpretation (not considered by Kanbara et al (2004)) the semiconducting sub-bands are not required to be ballistic.

While on the issue of ballistic transport and LL theory, the inclusion of a MWNT resistance in to the LL picture is conceptually awkward (Graugnard et al 2001), although there is little doubt in the quality of data fits after such a modification has been made.

The analytical expression for exponent in EG theory, e.g. equation (58) as used by Kanda et al (2004) and Bachtold et al (2001) is applicable only in the true 2D range. It underestimates exponents even when the mean free path is as low as 5 nm, which was the m.f.p. used by Kanda et al (2004) as lower limit, giving an exponent of 0.05, this compares poorly with Figure 3.32 from Egger and Gogolin (2002) were $l \sim r_{\text{int}} \sim 5 \text{ nm}$ and an exponent of 1.97 was extracted from the calculated $dI/dV$.

### 3.9.8.2 Energy Range of Power Law

While it quite easy to collate the energy ranges in the reported data there is often little information on what is outside the range of the presented data. The exceptions vary, for Liu et al (2003) the power law was only seen a limited range of the presented data all of which was explained with WL. Schönberger et al (1999) presented only the symmetric portion of the ZBA, ($< 20 \text{ mV}$), $dI/dV$ at higher voltages resembles the 1D DOS. However, it is comments within Kanda et al (2004) that highlight an important issue for on-substrate experiments. “For higher temperature measurement, however, we gave up measuring $IV$ characteristics, because the expected voltage range for the LL-like behaviour [Eq. (2)] was so high ($V > 7k_B T/e$) that the whole device might have been broken.” Eq. (2) refers to the nature of the power, $dI/dV \propto V^\alpha$ when $eV \gg k_B T$. The effort involved in sample preparation for these experiments is considerable; increasing the voltage or current range risks destroying the sample. It is worth noting however, that in Figure 3.35, from Bachtold et al (2001) the measurements range such that $eV/k_B T > 100$.

Where it is possible to extract from the reports the maximum current in the power law measurement it is of the order of $10^5 \text{ A}$. The results rarely portray a power law over several orders of magnitude. At best the $V^\alpha$ or $T^\alpha$ is shown over two to three orders of magnitude, in some cases such a Tarkkainen et al (2001) it’s a very small range indeed. However, uniquely in Tarkkainen et al (2001) the power law behaviour was
cut off by a transition to offset ohmic behaviour. The experimental arrangement has no significant differences with the others, and hence there is no obvious reason as to why Tarkiainen et al (2001) would observe a transition to offset Ohmic in an energy regime covered by all of the other reports.

Perhaps a reflection of this is the lack of justification for the origin of junction capacitance, assigning it to be from an average line capacitance arising from half the total length of tube. EQF is generally applied as it is in Bachtold et al (2001), such that the exponent arises from the $LC$ line impedance of the MWNT between the electrodes, the capacitance of the MWNT length overlapping the contact does not play a role.

### 3.9.8.3 Contact Resistances

The issue of a low contact or tunnelling resistance is a concern for the validity of all the ‘main contenders’ for an explanation, LL, EG and EQF theories. We can exclude the Boron doped MWNTs of Liu et al (2003) from this debate. The low two terminal resistance and hence implied low contact resistance is not an issue for the favoured WL based explanation in this case. But for Kanda et al (2004) and Graugnard et al (2004) it is a real issue. The requirement of ‘an electron tunnelling into the system through a barrier’ can be found for both for LL theory and CB, but it is only explicitly stated in terms of a resistance, for CB in Devoret and Grabert (1992), where a tunnelling resistance of at least $R_K$ is required. Nevertheless it is a reasonable benchmark for the existence of a tunnel junction rather than an adiabatic contact.

### 3.9.8.4 Conclusions

It is difficult to advance the analysis of many of the authors, often all that has been achieved is just to draw out some of the numbers facilitating a more direct comparison between the reports. Not all authors have examined the same possible explanations. An application of LL theory in some form is the only common element of the analysis within each paper.

A detailed reading of these papers brings out a number of issues:

- Low contact resistances, which threaten the validity of LL or CB, based explanations.
- LL theory is often applied incorrectly, with the assumption of only an outer shell participating.

What should be clear is that each report is quite different; taking into account the details of the observations within each report it becomes an almost impossible task to find one universal explanation. Although speculating on which theory might accomplish this task best, EQF has to be a good candidate due to the flexibility in defining the environment. Without all the details, there is however little to be gained from applying theories that the report’s author has not considered.

With the difficulty in defining an interaction strength it becomes difficult to rule out EG theory as in Bachtold et al (2001), who did so based upon the exponent predicted by the analytical expression. Conversely, it becomes difficult to conclude anything more definite than EG could explain the results, except in the case of Kanda et al (2004) where nothing in LL could reasonably be adjusted to produce the oscillating exponent, leaving EG theory as the explanation via elimination of LL.

If there is a trend for lower exponents in EG theory ($\alpha \sim 0.3$) to produce low upper limits for the power law behaviour then a transition to offset Ohmic behaviour should have been observed in Graugard et al (2001) and Bachtold et al (2001).
4 Results

Scientific experiments are ideally designed such that all but one independent experimental condition is constant. The outcome(s), or dependant variable(s) are then measured and the relationship between the dependant variable and the one independent variable that is being changed can at least be characterised with the goal of providing an explanation. Contacting a MWNT protruding from a polystyrene composite with a tungsten probe is certainly a repeatable experiment, and the experimental conditions are apparently constant. The results, however, are not completely constant; from tube to tube and even within measurements of the same tube.

For electrical conduction experiments, it is essentially resistance which is normally the dependent variable. Common parameters to change in order to elucidate the conduction mechanism are bias, temperature, magnetic field (direction and strength) and perhaps the preparation or condition of the material under test. For nanostructures the size of the sample is also a factor, as it can no longer be normalised.

The experimental set-up described in the following section allows only for the control of bias (current or voltage), while the other conditions listed above are either impossible to adjust or even monitor. With none of the usual means of isolating a particular conduction mechanism at our disposal the variation or 'quasi stability' in our results is an essential quality for determining the conduction mechanism. Even though it may not be in a perfectly controlled manner, at least one relevant experimental condition is changing; it is this, which can be used to test any proposed explanation. Besides the originality of the results, there is strong motivation for explaining the results from an experiment where the independent variable(s) is apparently uncontrolled. As the experiments which are a little closer to an
experimental ideal (e.g. as those in Chapter 3) have yet to fully explain the power law
behaviour observed in MWNTs.

4.1 Experimental Set-up

The experimental set-up enables us to extract both CVD and Arc discharge produced
MWNTs for electrical measurements. Nanotube samples are mounted on the stage
within the SEM, while CVD samples can be placed on the stage upon the substrate
they were grown. Arc discharge tubes are first prepared in a polymer (Watts et al,
2001), which is then cleaved before mounting in the SEM, where cleaving exposes an
edge from which nanotubes can be individually selected, Figure 4.1. Figure 4.2 shows
a schematic of the SEM chamber. Two chemically etched Tungsten tips (prepared
following the method of Ibe, 1990) are used to contact individual nanotubes. These
are attached to stiff sections of wire, in turn the wire is mounted onto the Piezo
sliders, providing a means to control the probe position with a 40 nm resolution.

Figure 4.1: SEM image of cleaved edge MWNT polystyrene composite.
Figure 4.2: a) schematic layout of the SEM Chamber, showing the electrical connections. b) A low magnification image showing the Tungsten wire tips in the tip holders. c) High resolution image showing the connection to a CVD tube.

The SEM (Cambridge instruments stereo scan 250 Mk III) has specified resolution of 7 nm (20 - 25 nm realistically) and therefore does not allow for accurate diameter determination due to the resolution of the images and the tubes cannot be focussed on sharply. This also restricts our ability to distinguish a rope of small tubes form a larger MWNT. Ropes can be positively identified, but single MWNTs cannot be positively
identified. Besides an obvious thickness for larger ropes there are several other observable signatures of a rope; a sharp change in brightness, dimming or apparent thinning along the length of the tube(s). In addition, where the rope enters the polymer it sometimes splits into its constituent tubes. When manipulating a rope, its formation is easily disturbed. In the conduction studies presented here, every precaution was taken to ensure the probe contacted a single MWNT, and in the following sections, it is assumed they are all single MWNTs.

4.2 Electrical Measurement Set-up

Two Keithley 237 source meter measurement units were used to perform electrical measurements and to aid the manipulation of the nanotubes. Figure 4.3 shows the measurement set-up. In the most commonly used mode, source voltage, measure current, the guard is maintained at the same voltage as the Hi terminal. This eliminates the measurement of leakage current, and the capacitive effect within the cables. Leakage currents and capacitive charging currents only flow from the guard to the outer ground shield. The co-axial guard is extended into the chamber, close to where the probes are mounted onto the Piezo sliders, shown in Figure 4.3.

![Figure 4.3: Electrical measurement set-up.](image)

There are three terminals within the SEM chamber, the stage and the two probes, any one can be chosen as the ground. Although for measuring a thermionic emission current, using a stage mounded tip, as a microscopic anode an output high must be connected to the stage,
Although a co-axial guard is employed in the cables and within the chamber, the final connections to the probes will have some capacitance to ground. The stepping of the voltage as the IV measurement proceeds generates a current, $i_{\text{lead}} = c_{\text{lead}} \times dV/dt$, due to the finite $dV/dt$. As a result there is a positive contribution to the measured current on the forward up portion of the cycle (0 V to $+V_{\text{max}}$) and a negative contribution as the voltage moves from $+V_{\text{max}}$ to $-V_{\text{max}}$. With a stable IV measurement this charging current can be averaged out. With unstable IV characteristics averaging is not suitable, but the charging current can often be identified. These charging currents are typically very low ($10^{-13} - 10^{-14}$ A) due to the slow speed of the measurement and the extensive guarding of the leads. Occasionally, these very small currents are relevant for the power law measurements, one example is featured later; Figure 4.25 where both the uncorrected and corrected results are shown.

4.3 Transmission Electron Microscopy Results

Having introduced the experiment, the transmission electron microscopy (TEM) results are presented before the electrical measurements, as this reveals exactly what is being measured. TEM is performed by attaching a tube to a probe in the usual manner, with couple of small changes. The probe is etched from smaller diameter wire, such that it can be easily cut once mounted on a TEM slot grid. Instead of attempting to contact the very end of the MWNT protruding from the composite, the aim is to contact the MWNT further down the tube such that a length of it is left on both sides of the probe. This allows examination of MWNT sections which have not had current passed through them, although it is possible these sections may have been exposed to high temperatures in the process of inducing failure in the section of tube connected to the composite.
Figure 4.4: TEM of undamaged tube. The polystyrene coating is ~14 nm thick. This image is close up of the longest MWNT shown in Figure 4.6.

Figure 4.4 and Figure 4.5 illustrate the central result from the TEM. The tubes studied here appear to be good examples of the high quality MWNTs produced by the arc discharge method, i.e. the material is similar to that used in studies of Poncharal et al (2002) and those featured in section 3.9. In addition, a polystyrene coating between 4 and 14 nm surrounds the MWNT.
Figure 4.5: This TEM image shows the polystyrene coating 3.8 to 4.6nm thick on a MWNT that has sustained currents up to 2µA.

Figure 4.4 shows a section of MWNT which has had no current passed through it, while the MWNT shown in Figure 4.5 has sustained currents up to 2µA, which is fairly low, compared to the current levels which typically induce failure. The thicker polystyrene coating shown in Figure 4.4 compared to that in Figure 4.5 should not be taken as an indication that electrical currents thin the polystyrene coating. Rather these TEM images and others are illustrative of a polystyrene coating that can have various thicknesses.

The tube(s) shown Figure 4.6 were the first samples prepared for the TEM, as a proof of principle for the technique. Consequently, the protrusion from the composite was not examined to try and determine if it was a single MWNT or a rope of two or more tubes. Figure 4.6 reveals it to be rope consisting of two tubes, it does, however, serve to confirm what is often suspected in the SEM, some protrusions from the composite are composed of more than one tube and that it is unlikely for both MWNTs to have the same exposed length. This means that if an effort is made to contact the end of a protrusion (which it usually is) then it’s probable that that contact is made only to a single MWNT. Thus, if the conduction is dominated by phenomena at the probe-MWNT contact, the existence of more parallel MWNTs further down the tube, (i.e. a rope) should have a rather limited effect. However, should the conduction be
dominated by the MWNT bulk or perhaps the composite-MWNT(s) contact the presence of a rope instead of a single tube may well have a much greater significance.

Figure 4.6: TEM showing two MWNTs encased in polystyrene, forming a ‘rope’. The polystyrene wetting the probe can also be seen.

The polystyrene coating shown in Figure 4.6 also shows a couple of noteworthy features. Where the MWNTs meet the probe, the polystyrene appears to have wetted the probe. Also, the encapsulation of the MWNT in polystyrene has been significantly disturbed. This may have been caused by the probe during the process of trying to achieve a contact in the optimum point, which would be not too close to the end of the MWNT in this case. It should also be pointed out that TEM also impacts upon the polystyrene, after extended periods in the electron beam the polystyrene coating appears to change, appearing thicker in some places, thinner in others. The TEM images shown here were collected early on, the aim being to make them as representative as possible of the virginal state of the polystyrene coating.
Figure 4.7: TEM and SEM of a MWNT measured between two probes, the MWNT was broken by pulling the probes apart, rather than by electrically induced failure. Unfortunately the much longer segment of tube connected to the right hand probe was not observable in the TEM. (a) High resolution TEM of the small length of tube visible in (c). (b) SEM of MWNT at the time of IV measurement. (c) Low Resolution TEM showing left probe coated, probably in etching salts.

The images in Figure 4.7 all belong to a series of measurements on a single tube, the measurements are featured in section 4.5.5.3, (p128, Figure 4.24 and Figure 4.25). The measurements were made with the left probe, the right probe was grounded. A power law was observed in the IV measurement, but with extremely high resistances relative to the other power law measurements (500 MΩ minimum). The coating shown on the probe in Figure 4.7c suggests an obvious explanation for the
exceptionally high resistance. In the course of measurements a transition to ohmic
behaviour observed, with a much lower resistance of 440kΩ (~0.0087 GΩ).

The lack of a polystyrene coating indicates the polystyrene layer either is not always
present on the MWNTs after cleaving or again its presence is not stable with current
(1µA in this case) or the temperatures induced by this current. The MWNT featured in
Figure 4.5 sustained higher currents, and has a polystyrene coating implying the lack
of polystyrene is not a direct result of the current. The temperatures of the two tubes
may be different as the thermal conductivity of the MWNT-probe contacts may be
quite different, so it could be indirectly related to the current. Dissipation within the
MWNT is not necessary for it to become hot, dissipation within the contact can quite
effectively raise the temperature of the MWNT if the contact has poor thermal
conductivity.

It is suspected that probes similar to that shown in Figure 4.7c do occur in the course
of the experiments, but are much less likely to have produced the results featured.
Occasionally, such coatings which are probably left over from the etching process are
observable in the SEM, in which case the probes are then washed again until clean or
simply discarded. Despite looking clean in the SEM, for some probes it can however
be difficult to establish an electrical connection to any tube, and again the probe is
washed or more likely discarded. This is why probes like that in Figure 4.7c with
apparently comprehensive coatings are unlikely to have featured with any regularity
in the electrical results presented later on. Electrical connections with probes such as
that in Figure 4.7c are very poor, so typically the probe would be discarded rather than
utilised in IV measurements.

4.4 Electrical Measurements: High Power

The most general description of the instability in the IV characteristic would be a
decreasing resistance as the measurements proceed; it is probable that this is linked to
the measurement methodology. Upon initially making mechanical contact to a
MWNT, conducting an IV measurement where either the current or voltage was
pushed to high values would typically destroy the tube. If the IV measurement was
voltage driven, negligible current is typically observed until the current increases
dramatically (if it is unlimited by the source) and then the MWNT fails in quick
succession. However, if many IV measurements are made, gradually increasing the
voltage range or current limit, the resistance is lowered without any dramatic unexpected failure.

In the early stages of the conditioning process, when the maximum current the MWNT was exposed to is ~1-2 μA, the IV characteristic typically resembles a power law. Once the MWNT has been exposed to higher currents, the IV characteristic often resembles that shown in Figure 4.8.

![Figure 4.8: Representative characteristics often observed after a connection has been exposed to high current levels (> 1-2 μA). IV characteristic shown in solid Blue, GV characteristic shown in solid Red.](image)

It is not really possible to ascertain much from the IV characteristics alone in Figure 4.8. Plotting the conductance, $G = I/V$, does however show a straight line at low voltage. The straight line region fit seen at low voltages (< 10 V) of the GV characteristic in Figure 4.8 is a common feature of the results and it's also similar to that observed by Poncharal et al (2002) and Liang et al (2004) in their reports of ballistic conduction. The same linear GV was also observed by Tsutsui et al (2005) who did not commit to an explanation based on ballistic conduction. However, there is a significant quantitative difference between the measurements here and the ballistic conduction reports, in both the minimum conductance, $G(V \to 0)$ and the gradient $dG/dV$. Figure 4.9 illustrates the variation in these two parameters extracted from the measurements; both the minimum conductance and gradient are shown with
logarithmic class intervals. Looking at the minimum conductance, our measurements give $G(V\to 0) \sim 0.001 - 0.1 \, G_0$, compared to 0.9 and 0.4 $G_0$ in Poncharal et al (2002) and Liang et al (2004), respectively. Tsutsui et al (2005) observes the conduction minimum to be in the range 0.3 to 1.6 $G_0$.

![Histograms showing the distribution of parameters extracted from the GV characteristics](image)

Figure 4.9: Histograms showing the distribution of parameters extracted from the GV characteristics, note the logarithmic intervals in both cases. (a) The conductance minimum, $G(V\to 0)$. (b) Gradient of the linear region of GV characteristic, $dG/dV$.

The GV characteristic is the result of a 1D-DOS dependant conductivity, conduction need not be ballistic, i.e. $G(V\to 0) \sim \to 2G_0$ (transmission coefficients $\to 1$). The shape of $G(V)$ is the result of a temperature smoothed DOS staircase (Poncharal et al 2002), the width of each step determined by the sub-band separation, which is in turn
dependant on diameter. The height of each step is dependant on the contact resistance $R_c$ which can be expressed in terms of a transmission coefficient $T_{\text{contacts}}$ and the conductance of the higher sub-bands which should be $2G_0 \times T_{\text{subband}}$, where $T_{\text{subband}}$ is the transmission coefficient in the sub-bands.

The minimum conductance is therefore defined as:

$$G(V \to 0) = 2G_0 \times T_{\text{contact}} \times T_{\text{metallic subband}}$$  \hspace{1cm} (59)

The components of the gradient are:

$$dG = 2G_0 \times T_{\text{contact}} \times T_{\text{semi subband}}$$  \hspace{1cm} (60)

$$dV = \frac{1}{2} \frac{\Delta E_{\text{subband}}}{2 \cdot r_{\text{cnt}}}$$  \hspace{1cm} (61)

For multiwalled carbon nanotubes $T_{\text{metallic subband}}$ has been shown by Urbina et al (2003) to be unity at room temperature for lengths at of least 1.4 $\mu$m, while Poncharal et al (2002) extracted a free path up to 200 $\mu$m for the metallic sub-bands, also at room temperature. In contrast, electrons in the semiconducting sub-bands have a finite coupling to long range disorder; therefore $T_{\text{semi subband}}$ is typically much smaller and will be dependant on the level of disorder and length too. Poncharal et al (2002) extracted a mean free path of 200 nm for semi-conducting sub-bands. If we assume that $T_{\text{contact}}$ is constant with voltage, the gradient can be normalised:

$$\left( \frac{dG}{dV} \right)_{G(V \to 0)} = \frac{T_{\text{semi subband}}}{1/2 \times \Delta E_{\text{subband}} \times T_{\text{metallic subband}}}$$  \hspace{1cm} (62)

If we make further assumptions, $T_{\text{metallic subband}} = 1$ and give a value for the diameter, the transmission coefficient of the semi conducting sub-bands can be extracted. Even without these further assumptions the normalised gradient is still a useful measure, the diameter (and hence $\Delta E_{\text{subband}}$) should not differ too significantly from tube to tube.

We can also expect the ratio $T_{\text{semi subband}} / T_{\text{metallic subband}}$ to be fairly constant as the level of disorder should not vary significantly and the lengths of the MWNTs are usually around 5$\mu$m. This is all borne out in Figure 4.10, which shows the distribution of the normalised gradients. The distribution narrows so much that linear class intervals are suitable, the mean normalised gradient is 0.24 $V^{-1}$. The normalised gradients of Poncharal et al (2002), Liang et al (2004) and Tsutsui et al (2005) are 0.25 $V^{-1}$,
0.43 \, V^{-1} and 0.24 \, V^{-1} respectively, which is in excellent agreement with the histogram in Figure 4.10 given the probable variation in disorder, length and diameter.

![Histogram showing the distribution of normalised gradients](image)

**Figure 4.10:** Histogram showing the distribution of normalised gradients $(dG/dV)\times G(V\to0)^1$.  

Both the considerable narrowing of the distributions and the actual values of the normalised gradient extracted, endorses the interpretation of the $IV$ measurements as 1-D DOS dependant conductivity, where the transport could be ballistic or quasi-ballistic.

However, not all of the high power $IV$ measurements look like Figure 4.8. The following figures show some deviation from the behaviour typified by the measurement in Figure 4.8. Figure 4.11 and Figure 4.12 still have a liner GV region and the measurement can be normalised and is included in the histograms. Figure 4.13 is an example of a measurement which cannot be included in the normalisation.
Figure 4.11: Asymmetric GV characteristic, where the minimum conductance occurs at V = 0.2 V rather than 0 V.

Figure 4.11 shows a GV characteristic in which the minimum conductance occurs around 0.2V rather than at 0V, within the 1-D DOS interpretation of the linear GV characteristic, this could be the result of a Fermi level shift. In a pristine MWNT the Fermi level is located where the metallic bands cross, equidistant between the conduction and valance band of the first semiconducting sub-band.
Figure 4.12: GV characteristic with saturation occurring at bias voltage of 4.7V.

The saturation in the conductance is a feature that has been observed in two of our samples characterised by a high conductance (comparing the scales, $G$ is an order of magnitude larger than the other $GV$ measurement shown in this section; μS rather than a fraction of a μS). In this MWNT (Figure 4.12) the conductance saturation occurred at 4.7 V and in the other sample (not shown) it was at ~6.3 V, with a current of 17 μA (at the conductance saturation voltage of 6.3 V). It is possible that this saturation has the same DOS based origin as that in Liang et al (2004) where it occurred around 6V too. The conductance saturation occurs as there are no further sub-bands opening up.
Figure 4.13: $GV$ characteristic showing a conductance dip at 0 V, $G(V \to 0) \to 0$ and hysteresis.

In Figure 4.13 the arrows seem to indicate that the hysteresis is due to capacitive charging currents. It is possible to define a capacitance and correct for charging currents based on $dV/dt$ (the measurement is time stamped). The capacitance would have to be of the order of 100 nF. However, this fixed capacitance correction still does not fully eliminate the hysteresis. In addition, the value of capacitance is also at odds with those found where a capacitive charging current correction has been applied successfully. For power law data shown in Figure 4.25, p130 the capacitive charging current arises from a capacitance of 1pF, where the configuration of the probes is not that different. Given all this, the hysteresis is probably real; it was a consistent feature from one measurement to the next, along with a conductance dip at 0 V and a linear $GV$ at low voltage, although the specifics of each characteristic were not stable. The conductance dip at 0 V could be speculatively explained within the 1-D DOS dependant conductivity as the absence of metallic sub-bands.

Another series of measurements made on a MWNT connected with two probes and to the composite showed a linear $GV$ characteristic when measured from each probe to the composite and between the probes. All $GV$ characteristics gave quite different $G(V \to 0)$ and $dG/dV$ values, but once normalised to the minimum conductance the gradients were consistent.
The assumption of a voltage independent contact conductance even at high voltages is perhaps reasonable, where the overall conductance is high and $GV$ closely replicates the 1-D DOS, i.e. saturation is observed (Figure 4.12). In cases where the conductivity is low and the voltage range is large, e.g. Figure 4.8, it is probable that the contact resistance is not constant at high voltages and this could be the cause of an enhanced conductivity at high voltage (i.e. the super-linear increase in conductance). This enhanced conductivity at high voltage could also result from increased participation from the inner shells of the MWNT; such participation from the inner shells is only possible if the MWNT is not an ideal ballistic conductor. If it is, there would be no voltage drop between adjacent shells to drive inter-shell currents.

Ultimately the low values of conductance relative to $2G_0$, the variation in conductance and the inconsistencies between the measurements make it impossible to elucidate a complete picture of the conduction mechanism in our MWNTs, in the high power regime. However, the narrowing of the distribution of results created by normalising the gradient strongly indicates it is the right approach; the numerical agreement with 1-D DOS is also extremely good. 1-D DOS dependant conductivity can also explain the deviations from the typical measurements, although with individual expectations this part of the explanation can never be perfect. In conclusion, a one dimensional DOS dependant conductivity is consistent with our measurements.

**4.5 Electrical Measurements: Power Law Data**

The $IV$ results in the previous sections are not particularly new, and offer little new insight into the conduction in multiwalled carbon nanotubes that have not already been demonstrated elsewhere. Some key aspects of the observations are consistent with other MWNT conduction experiments. In this section however the results are new, and through the analysis in section 5.5.1 offers some insight into conduction in MWNTs.

At the very outset of this chapter it was outlined that this experiment is far from the ideal scientific experiment, where all relevant conditions can be controlled and measured. Given the lack of control and the variation in the results there are two separate tasks:

1. Identify any consistent aspect of the results and patterns in the variation of the results.
2. Identify experimental conditions which may vary.

Only after this can an explanation be formed and tested. The following subsections are all concerned with the first point; there are two consistent aspects of the results, before large currents (~1-2μA) are passed through the MWNT. The IV characteristics often show power law behaviour and offset ohmic behaviour. The best of these results are presented in sections 4.5.2 and 4.5.3, and the suitability of the offset ohmic fits is discussed. Having identified consistent aspects of the results, the variations are then explored in section 4.5.5. Finally, a pattern in the variation of the results is identified. Before the fits themselves are presented, the equations used to fit the data are given in the following section.

### 4.5.1.1 Equations Used in Data Fitting

The IV data has been fitted to the phenomenological form of the energy dependant power law, from Yao et al (1999): -

\[ I(V) = C_1 \cdot T^a \cdot V \left( 1 + C_2 \cdot \left( \frac{e \cdot V}{k_B \cdot T} \right)^a \right) \]  \hspace{1cm} (63)

Where \( C_1 \) and \( C_2 \) are fitting parameters and all of the other symbols have their usual meanings. \( T \) was fixed at 300 K, the experimental condition. Equation (63) is a general equation for an energy dependant power law, giving \( I \propto V^a \) at low voltages (seen as a slope of gradient 1 on log-log axis) and \( I \propto V^{a+1} \) at high voltages (seen as a slope of gradient \( a+1 \) on log-log axis). The power law as specified in environmental quantum fluctuations theory (EQF), Ingold and Nazarov (1992), and Devoret et al (1990) is given by: -

\[ I(V) = \frac{\exp(-2\gamma/g)}{\Gamma(2+2/g)} \cdot \frac{V}{R_F} \left[ \frac{\pi eV}{g Ec} \right]^{2g} \]  \hspace{1cm} (64)

Where, \( \gamma = 0.577... \) is Euler's constant, \( R_F = h/e^2 \), and;

\[ g = \frac{R_F}{Z} \]  \hspace{1cm} (65)

Equation (64) was derived for the zero temperature case, so there is no region where \( I \propto V^1 \). The exponents in equations (63) and (64) are related to each other by: -
The offset ohmic characteristic is given by:

\[ I(V) = I_0 - \frac{e}{2C_f \frac{V}{R_f}} \]

Equation (67) is the ideal offset ohmic, and is only accurate when \( Z = \infty \) in a single junction. The transition from the power law suppression of the blockade at low voltages to offset ohmic characteristic in equation (67) is given by:

\[ I(V) = \frac{1}{R_f} \left[ V - \frac{e}{2C_f} + \frac{g}{\pi^2} \frac{e^2}{4C_f^2} \frac{1}{V} \right] \]

Equation (68) possess a term \( \propto V^1 \), which provides the correction to equation (67). Equations (64) and (68) should together, seamlessly account for the IV characteristic, (at least for \( T = 0 \) K), meeting at \( E_C \). However despite sharing a page in Ingold and Nazarov (1992) they do not meet, with the voltage independent pre-factor in equation (64) being slightly too large. Due to this minor quantitative enigma with equation (64) and its zero temperature assumption, the phenomenological power law, equation (63) was used fit the power law data. Equation (67), the simple offset ohmic characteristic was used to fit the high voltage deviations from power law behaviour, which is reasonable because at high impedances the difference between equations (67) and (68) is small. The fits are however often shown with equation (68) as it follows the data better at \( eV \approx E_C \).

### 4.5.2 Power Law Fits

A fairly typical power law result is shown in Figure 4.14, where a correction for current offset of \( 7.5 \times 10^{-13} \) A has been made. After this correction, the low voltage portion of the measurement fits the \( I \propto V^4 \) part of the power law perfectly. This kind of correction to the measurement is only necessary when the current is near the limit of the measurement system. The \( I \propto V^{5+1} \) portion of the fit works for five orders of magnitude, as will become apparent from the many power law fits featured here this quality of fit over so many orders of magnitude is not uncommon.
Figure 4.14: Power law with a correction for current offset of $7.5 \times 10^{-13}$ A. Inset shows deviation from the power law at high voltage. Dashed Green – original measurement, Solid Black – corrected measurement and dotted Red – power law fit with $\alpha = 5.16$.

Figure 4.14, more specifically the inset shows another common feature of our results, deviation from the power law at high voltages. In the following section, it is shown that this deviation from the power law fits an offset ohmic characteristic. However in Figure 4.14 the measurement does not go beyond 10 V, and consequently there is not a large enough region at high voltage to enable a really confident fit to any equation. If one extrapolates beyond the limits of the measurement in Figure 4.14, the current would soon be in the $\mu$A range and the voltage very large ~ 20 V. This would correspond to quite high power levels and most likely change IV characteristic altogether, so that it would resemble those shown in section 4.4. It is this scenario which makes the ‘perfect’ IV measurement elusive, the perfect IV for data fitting should have a power law region stretching over many orders of magnitude and a high voltage deviation which continues for at least two or three times $E_C$. Hence a measurement which consists of a significant deviation from the power law, does not generally have large power law region, but given the number of measurements like that in Figure 4.14, the other measurements with smaller $I \propto V^{\alpha+1}$ regions can confidently be interpreted as a power law.
Figure 4.15: A measurement fitted by a power law at low voltage and offset ohmic at high voltage. Solid black line; measurement. Red dashed line; power law fit with equation (63), $\alpha = 5.4$ (equivalent to $Z = 65$ kΩ). Blue dashed line; offset ohmic fit with equation (68), same value of $Z$, $C_J = 1.3 \times 10^{-19}$ F and $R_T = 1.3 \times 10^4$ Ω.

Figure 4.15 is an example of one result where the balance between power law and offset is quite good. This time the offset ohmic is also shown, and fits the data perfectly.

Power law fits can be described as symmetric, as far as they are stable. That is to say, stable measurements are generally symmetric (Figure 4.16), but the less stable measurements are not perfectly symmetrical. The asymmetry is probably a reflection of the instability, consistent asymmetry is rare.
Figure 4.16: Probe-to-probe symmetric power law measurement. Solid black line - average of the forward portion of the $IV$ measurement. The dashed red line is the average of the reverse portion of the measurement. The measurement is well fitted by an exponent, $\alpha \approx 3.7$. The averaging was applied as not to clutter the forward and reverse comparison by presenting 4 traces, the procedure also cancels out any charging current, no correction for a current offset has been applied.

4.5.3 Offset Ohmic Deviation

The deviation from the power law at high voltages was shown in the previous section, and the fits were good. But, an offset ohmic fit should really be judged on a linear-linear scale. Figure 4.17 is the same as Figure 4.15 but with a linear-linear scale, the fit still looks good, but the instability in the $IV$ measurement is more noticeable.
Figure 4.17: Same data and fits as in Figure 4.15 on a linear-liner scale. Dashed red line; power law and dashed blue line; offset ohmic. The measurement is in solid black.

The offset ohmic fits shown so far have based on equation (67), the ideal offset ohmic characteristic, exact in the limits for \( Z = \infty \) or for \( V \to \infty \) if \( Z \neq 0 \). But as \( Z > R_F \) in Figure 4.17 the ideal offset ohmic form, equation (67) works well. A low impedance, (small exponent) is necessary to demonstrate the difference between equation (67) and equation (68). Equation (68) properly accounts for the transition form the power law regime \((eV < E_C)\). This is shown in Figure 4.18, where both equations are shown. Values of \( R_T \) and \( C_I \) are the same for both equations and the impedance used in equation (68) is that extracted from the power law region. The excellent fit of equation (68) not only confirms it is the right form of equation for the data, but also that the power law exponent (impedance) has been correctly extracted from the power law region.
Figure 4.18: Comparison of offset ohmic fits. The measurement shown in solid black, the simple offset ohmic fit, equation (67) shown by the red dashed line, and the offset ohmic transition, equation (68) is shown by the green dot-dash line. An impedance of 7.7 kΩ used in (68) was extracted from the power law region.
Figure 4.19: Normalised offset ohmic characteristics, with $R_T = 1$ and $E_C = 1$. The theoretical predictions for the extreme cases are shown by the dashed grey line ($Z = 0$, giving ohmic behaviour $I = V$) and the solid black line ($Z = \infty$, giving offset ohmic behaviour, equation (67)). The actual measurements are shown in solid colours, with the extracted impedances; 7.7 kΩ (Red), 27.7 kΩ (Green), 48.9 kΩ (Blue), 57.3 kΩ (Cyan) and 65.0 kΩ (Magenta).

Once fitted to the offset equation (67), the junction capacitance and the tunnel resistance can then be normalised out from the IV characteristic. The only difference between the IV measurements should then be the impedance, $Z$. The normalised IV characteristics for a single MWNT is shown in Figure 4.19, which clearly demonstrates how for low impedances (red and green) the coulomb blockade is suppressed and large currents are seen below $E_C$. In contrast the high impedance measurements (blues, cyan and purple) cling to the offset ohmic characteristic (solid black). The low impedance measurements also take longer to collapse onto the offset ohmic characteristic, as predicted by equation (68).

Not all of the measurements in Figure 4.19 collapse onto the offset ohmic characteristic as expected, i.e. from $V \sim E_C$ to the end of the measurement,
specifically the measurements shown in blue and cyan. Although they do fit the offset ohmic characteristic, they deviate from it around $1.8 \ E_C$. In fact the measurements shown in green and red also do this at 6.0 and 9.7 $E_C$ respectively which is off the scale in Figure 4.19. A straight line (solid light grey) with a gradient > 1 and voltage-axis intercept > $E_C$ fits the deviation well. This deviation, how best fit it and interpret it is explored in the next section, 4.5.4.

4.5.4 Suitability of Fits

Figure 4.20 is a typical example of the choices presented in fitting the data in an offset ohmic regime. The measurement in Figure 4.20 is shown fitted to two offset ohmic characteristics, equation (67) both providing a good fit in different voltage regimes. However, in the case of Figure 4.20, a single fit can be made to work in both of these voltage regions, using equation (68) with the values of $C_J$ and $R_T$ from the high voltage fit (red) and a relatively small impedance, ($Z \sim 6.45 \ k\Omega$), provides an appropriate fit. This is because a lower value of $Z$ in equation (68) provides a more gradual transition between the power law region ($V < 0.5$) and the offset ohmic characteristic.

![Figure 4.20](image)

*Figure 4.20: Solid Black – Measurement. Solid Blue - Low voltage fit, ($E_C = 0.28 \text{ eV}$ and $R_T = 1.07 \text{ M}\Omega$). Solid Red - High voltage fit, ($E_C = 0.55 \text{ eV}$ and $R_T = 0.847 \text{ M}\Omega$).*
There is an obvious problem interpreting the result with the later data fit (equation (68)). In order for the power law and offset ohmic regions to meet, Z has been lowered from 27.7 kΩ, (extracted from the power law region) to 6.45 kΩ. Later an important plot, Figure 4.29, shows the relationship between Z and $C_j$. For the data points that form Figure 4.29, three other measurements, in addition to that shown in Figure 4.20, present this choice in interpreting the data. All of them require a much smaller value of Z to be used in equation (68), ranging between a quarter and three quarters of the value extracted from the power law fit. They are not all close to $R/T/4 - 6.4$ kΩ, a significant resistance for carbon nanotubes. There is no correlation of this lower value of Z with other parameters extracted from the fits. As mentioned previously, the single fit works well for the measurement in Figure 4.20, but for some of the other data sets a single data fit is a poor substitution for the two offset ohmic fits based on equation (67).

The quantitative treatment of the tunnelling process is non-trivial, and strongly dependent on the size and shape of the potential barrier. Coulomb blockade adsorbs all of the details of tunnelling into a single parameter the tunnelling resistance $R_T$, assumed to be voltage independent. In general terms, the shape of a tunnel barrier is distorted with the application of an electric field. However at high fields the shape of tunnel barriers significantly distorts and the effective width may also reduce. Even with some uncertainty with regard to the width of the tunnel barrier between the MWNT and probe, it is probable that the electric field is high (that is in terms of fields that would distort a 15 nm tunnel barrier, with 1V, giving a field of 66 Vμm$^{-1}$). Given the high value of the electric field it is difficult to argue that $R_T$ should be constant. However, a simple change of $R_T$ would not reproduce the fit seen in Figure 4.20 as it has a different intercept. If $R_T$ were to become voltage dependent above a threshold voltage, $V_{TH}$, this would reproduce the second offset ohmic fit. The threshold voltage for change over, $V_{TH}$, plotted against the coulomb gap of the low voltage fit shows a reasonable correlation (Figure 4.21), and would suggest why no $V_{TH}$ is observed in the highest impedance measurement, where the coulomb gap is 0.61 V. As can be seen from Figure 4.21 the expected value for $V_{TH}$ in this case is approximately zero, which is well below the coulomb gap. Therefore, if this is a real trend, a single fit would be expected, although it may have an artificially high coulomb gap (small $C_j$) and an artificially low $R_T$. 

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Figure 4.21: Coulomb gap vs. threshold for voltage for the change in offset ohmic characteristic. The coulomb gap is that extracted from the low voltage offset ohmic fit. Another way to view the coulomb gap is the extent of the power law region. In the case of the highest impedance measurement, the power law region extends to ~ 0.6 V, whereas the pattern suggest that $V_{TH}$ would be less than 0.6 V, explaining why no $V_{TH}$ was observed for the highest impedance measurement.

In conclusion, using a single fit (equation (68)) with a differing value $Z$ to that extracted from the power law regime is clearly an undesirable choice as it does not always give an appropriate fit, whereas two fits with equation (67) always works. Furthermore, the single fit (equation (68)), produces no pattern in the fitting parameters, whereas as the two fit method does (Figure 4.21).

4.5.5 Stability of the Measurements

This section first shows just how the exponent can change, with a fairly typical result where the exponent reduces within a single measurement cycle. Other observations are also detailed which contribute to the analysis by providing tests for any prospective explanation, these observations play a crucial role in locating the power law behaviour.
4.5.5.1 Changing of the Power Law Exponent

An IV measurement will always be limited, by either the maximum voltage or current permitted by the source measure unit. In order not to destroy a MWNT during the initial stages of the experiment, the first measurements are usually made with rather low values for the maximum voltage and current, gradually whichever one is limiting the range of the IV will be increased. This gives a series of IV measurements on a single MWNT with ever increasing ranges. If the act of measuring the MWNT had no effect each IV measurement would give an identical result. This is not always the case, and so the IV measurement range is increased only once the result appears to be stable. This means after three consistent measurements. In general, the IV measurements can be described in two ways:

1. Those well described by a power law and often with an offset ohmic region, e.g. Figure 4.14, p116.
2. Those well described by a linear conductance-voltage (GV) relationship, e.g. Figure 4.8, p106.

The change from an IV described by a power law to that with a linear GV relationship is the most dramatic change. Less dramatic but just as sudden changes also occur when a power law describes the IV characteristic.

The observation of a power law \( I \propto V^{\alpha - 1} \) in the IV measurement is a consistent aspect of the results, with the actual exponent \( \alpha \) which describes the power law being only 'quasi-stable'. Typically, for many sequential measurements on the same MWNT the exponent is stable, but the exponent can change in the course of the measurements. This happens quite suddenly, Figure 4.22 shows a good example of how this happens in the course of one single IV measurement. The change in this case was not brought about by moving either the probe or stage. The end result is that a MWNT may typically exhibit one or two exponents before failing, or, show 'high power', linear GV type behaviour, discussed earlier in this chapter, section 4.4.
Figure 4.22: Change in exponent during one measurement. The dotted black lines are power law fits (63) with exponents noted adjacent to the curves. In order of the IV measurement cycle; Navy blue – Forward up, Pink – Forward down, Orange – Reverse up and Olive Green – Reverse down.

Figure 4.22 shows one IV measurement broken down into four constituent parts. IV measurements are conducted in this manner so that the capacitance within the measurement system can be identified and corrected for, when the measurement is stable. The pink (forward down, negative $dV/dt$) measurement clearly passes through zero at 0.4 V. Comparing the pink and blue (forward up, positive $dV/dt$) at low voltages shows the difference is most probably related to the charging of measurement system capacitance. At higher currents $10^{11} - 10^8$ A, where charging currents are irrelevant, there is a similar instability in both the forward down (pink) and reverse up (orange), compared to the consistent power law that characterised the first part of the measurement cycle, the forward up (blue). Despite this instability, the ‘unstable’ portions of the measurement cycle do agree well with a power $\alpha = 3.2$ power law at higher current levels. It is when the current has reached the limit of 1 $\mu$A, imposed by the instrument, between the reverse up (orange) and the reverse down (green) that something appears to change and reverse down characteristic is well fitted with a different exponent, $\alpha = 2.3$. The current at low voltages becomes an order magnitude larger than the capacitive currents.
4.5.5.2 Contacting Different Parts of the Same MWNT

Figure 4.23 shows two IV measurements gained from the same MWNT, each from one probe to the polymer composite. Significantly different exponents are seen for different probes.

![Graph a) with exponent α = 1.9 and graph b) with exponent α = 3.6](image)

Figure 4.23: Different exponents observed with a different probe. a) The first connection to the right probe, with exponent, $\alpha = 1.9$. b) The second connection to left probe gives an exponent, $\alpha = 3.6$. The SEM shown in the inset shows the MWNT connected to only the left probe as this image was clearer than the one showing the MWNT connected to both probes, which was the condition when the measurement was made. Scale bars are not included on the SEM image inserts, but the length of exposed MWNT is 5 µm.
Figure 4.23 shows the polymer composite is not responsible for the power law behaviour. Neither the current pathway in the polymer-MWNT composite or the contact where protruding MWNT meets the composite has changed and therefore cannot be responsible for the change in the power law exponent. This leaves only the MWNT bulk or MWNT-probe contact as the origin of the power law.

4.5.5.3 MWNT Between Two Probes

This is another measurement that supports the assertion that the polymer composite does not influence the power law behaviour. By measuring between two probes the there is no longer a current path in the polymer composite, but before that measurement is presented, initially probe-to-probe measurements were made while the MWNT was still embedded in the composite at one end, Figure 4.24.

![IV measurement showing asymmetry in a measurement of the MWNT section between two probes. Despite the asymmetry, the same exponent, $\alpha = 3.65$ is seen for forward (wine red) and reverse (Olive Green) characteristics. Inset shows the electrical measurement configuration. Generally the $IV$ characteristics can be said to be as symmetric as they are stable (stable meaning repeatable). Figure 4.24 shows what can be considered an exception to the symmetric behaviour generally seen in the $IV$ measurements. It was the first of a series of measurements on a MWNT contacted with two probes, while one end was...](image-url)
still embedded in the polymer composite. The source-meter unit connected to the composite was set to zero current, voltage meter mode and the measurement was on the left probe with the right probe grounded. The complete IV measurement is shown, uncorrected for the any charging or offset currents. The forward and reverse characteristics show the same exponent, $\alpha \sim 3.64$, but there is a consistent difference in the current of about half an order of magnitude. This difference can be entirely explained in BQF with different tunnelling resistances, $R_T$ for forward and reverse bias.

After a further fourteen IV measurements, the power law is still characterised with an extremely high resistance but with a higher exponent, $\alpha \sim 5$, this time the IV was stable enough to apply corrections, Figure 4.25. In the time between the measurements in Figure 4.24 and Figure 4.25, the probes were corrected for drift and the section of the MWNT connected to the composite was broken. Both of which could have impacted upon the exponent. The electrical connection after adjusting for drift was particularly poor, but a fit based on two orders of magnitude, gives $\alpha \sim 6$. Measurements just after the disconnection to the polystyrene composite are consistent with Figure 4.25 i.e. $\alpha \sim 5$. 
Figure 4.25: Dashed olive green line shows the uncorrected up and down IV for the MWNT. Solid black line - averaged up and down, an offset current of 6.5x10^{-14} A. Dotted Red line - power law fit $\alpha = 4.95$. The power law fit shown was made interpreting the dip in current between 10-15V as the result of a quasi-stable tunnelling resistance, $R_t$, increasing between 10-15V. An alternative based on satisfying all data points gives $\alpha \sim 4$ and a fit that underestimates the current at the highest voltages. Inset shows the electrical measurement configuration.

The measurements shown here also serve as an example that occasionally the exponent does increase in the course of the measurements, which is the opposite to the general trend observed in the results.

4.5.5.4 Mechanical Instability

With the stage and probes mounted separately in the SEM chamber drift between the two is a constant problem. It can be mitigated by techniques such as leaving probes in the vicinity of a MWNT for a hour or two, allowing the system to relax before making the fine movements necessary to mechanically contact a MWNT. Also the probes and the stage can be carefully adjusted when in contact with a MWNT, although this is not really desirable for a number of reasons, both scientific and practical.

MWNTs are fairly rigid (Hertel et al 1998), this can also be inferred from Figure 4.1, where for the most part the MWNTs protrude in straight lines from the cleaved edge.
of the polymer composite. However, they can and do bend. Generally, MWNTs are attracted to the probe, and a small voltage (~ 1 V) on the probe can encourage this further. So, when a mechanical connection to the MWNT is made, the tube has already moved from its ‘natural’ position. The probe is then usually moved to confirm the mechanical connection (the MWNT should also move), before being returned to a position which appears to maximise the visible length of the MWNT and minimise the stress/strain that is placed on the tube. The gradual stage drift can then increase the stress/strain on the MWNT, until the point at which the MWNT springs off. If the probe is still relatively close, or has sufficient voltage on it, the MWNT can re-attach instantly in a different position. This is exactly what appears to have happened at ‘Event #1’ in the final measurement of one MWNT shown in Figure 4.26.

![Figure 4.26](image)

**Figure 4.26**: Mechanical instability shown in an IV measurement. Inset shows the same measurement on a linear-linear scale. Looking at the inset for the offset ohmic fits, initially a Coulomb gap of 1 V is seen with $R_T = 1.40 \, \text{M}\Omega$. After Event #1, another fit indicates a Coulomb gap of 1.73 V and $R_T = 1.86 \, \text{M}\Omega$. Besides the dramatic mechanical instability labelled as events the measurement is also plagued by less significant instabilities, despite this it is still possible to measure a approximate exponent of $\alpha = 3.86$ as indicated by the grey line.
Event #2 corresponds to the MWNT detaching from one probe and then reconnecting, the reconnection is to the 2nd probe which is also in the vicinity of the MWNT's natural position. Not all mechanical instabilities are as dramatic as that shown in, Figure 4.26. In section 4.5.5.3, it was noted how the exponent appeared to change after making a slight adjustment to the probe.

4.5.6 Patterns in Fitting Parameters

The previous sections have all been about establishing consistent aspects of what superficially appeared to be inconsistent results. In qualitative terms, a power law is consistently observed before a large current has passed through the MWNT. Deviation from the power law at high voltage is also seen in many samples. For measurements that extend some way into the high voltage deviation from the power law, the deviation has been shown to take an offset ohmic form. The exponents are large compared to those previously reported from both SWNTs and MWNTs in chapter 3.

4.5.6.1 Exponent and Probe Size

Rather than show a histogram type distribution of exponents, they are shown in Figure 4.27 as function of the probe diameter. There is a possible influence of the probe size on the exponent. Not necessarily a correlation, but for small probe sizes there appears to be a greater probability of higher exponents and vice-versa for larger probes. However, with the removal of a couple of points, e.g. that the one at ~ 800 nm any such probe size-exponent relationship is imperceptible. From this data, it is not definitive that the probe size has an influence on the exponent.
Figure 4.27: Exponents vs. probe diameter. Initial exponents - open black squares (□), secondary exponents - solid red circles (●) and further exponents - green plus signs (+).

Figure 4.27 also shows another important aspect of the results, the variation (in the exponent, $\alpha$) seen in one MWNT, (intra-MWNT variation) is comparable to the inter-MWNT variation. This is an important observation; the consequences are discussed later in section 5.1.1.

Having introduced the probe size as a possible variable, it should be properly defined. The probe size is intended to be a measure of the size of the metallic body in the vicinity of the MWNT contact. Figure 4.28 shows how the probe radius or diameter is defined as the length of the MWNT overlapping the probe. By far the most common type of contact is that illustrated in Figure 4.28b, where the probe axis and MWNT axis are almost normal to each other. In fact, it is this situation which is approximated in the calculations featured later in the explanation, where the same definition of probe radius is used.
Figure 4.28: Probe radius definition, with two contact geometries. In both cases it is possible to define the length of MWNT 'above' the probe. a) Probe axis and MWNT axis almost parallel. b) Probe axis and MWNT axis almost perpendicular to each other.

4.5.6.2 Exponent and Junction Capacitance Relationship

The quasi-stability of the system usually leads to one or two exponents being observed in the lifetime of the measurements for a particular MWNT. There are however occasions where several exponents are observed from a single MWNT. The MWNT identified by a connection to the ~1000 nm probe in Figure 4.27 showed five different exponents in the measurement lifetime and the IV characteristics are fairly stable, i.e. they can be fitted and interpreted with confidence, in both the power law and the offset ohmic regions. Figure 4.29 shows the impedance, $Z$ extracted from the
power law region ($\alpha = 2Z/R_f$) to junction capacitance that is extracted from the offset ohmic fits. For four of the measurements, two offset ohmic fits could be made. In Figure 4.20, the measurement corresponding to the points is $Z = 27.7$ k$\Omega$. The value of capacitance extracted from both fits is shown. All of the IV measurements from which Figure 4.29 has been created from have been shown, previously. They are all shown together, normalised in Figure 4.19. In addition, Figure 4.15, and Figure 4.17 correspond to the point with the highest exponent or impedance.

![Impedance vs. $1/C_j$](image)

**Figure 4.29: Impedance, Z vs. $C_j^{-1}$.** Solid blue circles show extracted impedance vs. capacitance values extracted from the low voltage fits. Open red squares are the extracted impedance vs. capacitance values extracted from high voltage fits. The point at 65 k$\Omega$ only showed a single offset ohmic fit, and has been included in the series ‘high voltage fit’. The solid grey line shows a fit to the 4 points from low voltage fits ($R^2 = 0.997$). The dotted grey line is a 5 point fit if the 65 k$\Omega$ point is included ($R^2 = 0.919$).

A straight line fit between $Z$ and $C_j^{-1}$ with the capacitance values extracted from the low voltage offset ohmic fit is obvious. The quality of the fit is not as good if the 65 k$\Omega$ point is included, further suggesting that in Figure 4.21, the 65 k$\Omega$ measurement should be interpreted as a ‘high voltage’ fit. In any case a strong relationship between $Z$ and $C_j^{-1}$ is observed, with increasing impedance for smaller junction capacitances.
4.6 Results Summary

The TEM has shown the arc-discharge produced MWNTs to be good quality material which is covered in a polystyrene coating. A series of IV measurements have been made on single polystyrene coated MWNTs with ever increasing ranges (i.e. the maximum current and voltage). Together with mechanical movement, the use of increasing maximum current and voltage brings about changes in the IV characteristics. Initially, the IV data fits well to a power law, often with an offset ohmic region at higher voltages. Quantitative changes in the IV data occurs, with the parameters that describe the power law fit ($\alpha$ or $Z$) and the offset ohmic fit ($C_j$ and $R_p$) changing. Detailed analysis of a MWNT that showed several such quantitative changes in the IV characteristic reveals a relationship between the exponent, $\alpha$ (to which the extracted impedance, $Z$ is proportional) and the junction capacitance $C_j$. Although the exponent(s), $\alpha$, varies from one MWNT to the next, a similar range of variations can be shown in single MWNT.

When the maximum current reaches a certain level, typically 1 – 2 $\mu$A, a more dramatic, qualitative change in the IV characteristic occurs. The IV fits a linear conductance-voltage characteristic that is interpreted as 1-D DOS dependant conductivity. This is despite the contact resistance remaining high relative to the resistance of a ballistic MWNT, 6.4 k$\Omega$. 
5 Discussion of Conduction Results

In the previous chapter numerous IV measurements were presented, they were divided into two groups, high power data and power law data. Although primarily a results chapter some preliminarily analysis was applied to the high power data. It showed the high power measurements were equivalent to some of those featured earlier, in chapter 3, and thus could be explained as a consequence of the MWNT’s 1D electronic structure.

Despite the remaining low power data being accurately described by a power law, it could not be described as equivalent to the work reviewed in chapter 3. Indeed not all of the power law reports of chapter 3 could be described as equivalent. Moreover, even if they could be it would not straightforwardly lead to a single, unifying explanation.

This chapter is therefore devoted to an explanation of the power law data featured the previous chapter. The unique aspects of the results requiring an explanation are the:

- Variable and high exponent values,
- The relationship, \( Z \propto C_f^{-1} \) shown in Figure 4.29.

Additionally, any explanation needs to be consistent with the experimental observations, such as those in section 4.5.5. (e.g. those that indicate the power law originates from the probe-MWNT contact)

It is possible to identify a wide range of experimental conditions that may be the source of the variety and instability of the results. The first part of this chapter, section 5.1, is focused on comparing these conditions to the experimental observations of how the exponent behaves. This process aids in the forming and testing of any explanation.
5.1 Analysis of the Exponent Behaviour

The exponent behaviour is well documented in section 4.5, so the first task is to identify any experimental conditions which may be varying. This list has the potential of being very long and, so it is necessary to limit it at the outset. The observations in sections 4.5.5.2 and 4.5.5.3, both independently provide strong evidence that the MWNT-polystyrene composite is not the source of the power law behaviour. Therefore, we follow explanations based on the MWNT bulk and or the MWNT-probe contact.

5.1.1 Intra and Inter MWNT Factors

The experimental conditions which may be varying and subsequently influencing the exponent can be organised into two sets; intra and inter tube factors. Exclusively, inter tube factors include the number and character of the shells, the diameter etc, as its impossible for these to vary within a MWNT (unless we are pealing them as in Collins et al (2001), but there is no evidence for this in our case). The intra-MWNT factors are entirely a subset of inter MWNT factors, e.g. the polymer thickness; it's likely that this is not constant in the course of the measurements, and is bound to vary from tube to tube as well. Other factors are less easy to place, with disorder an exclusively inter tube factor unless the act of measurement creates disorder in which case it would be intra-tube factor as well. This is all shown graphically in a Venn diagram, Figure 5.1.
Factors Influencing the Exponent

**Inter**
Could vary between MWNTs
- Diameter
- Length
- Number of shells
  - Character (and mix) of shells
- Probe size

**Intra**
Could vary within the same MWNT
- Polystyrene thickness
- Stress or strain in the MWNT*
- Effective probe size*

*change caused by gradual mechanical movement

Figure 5.1: Venn diagram illustrating factors that influence the exponent.

The fact that the variation in a single MWNT (1000 nm probe, Figure 4.27) covers almost the entire range of exponents found would suggest the exponent or impedance is predominantly determined by intra tube factors. This means that regardless of whether Figure 5.1 is considered complete or not (that is in terms of possible factors), exclusively inter tube factors can be ruled out as dominant factors in the variation of the exponent.

5.1.2 Dynamic Exponent Behaviour

Having ruled out length, diameter, probe size and the number of shells we are still left with several intra tube factors to consider. To further eliminate from the list of possible experimental conditions/factors that may not be constant, the likely behaviour of the experimental conditions in general terms is compared with the exponent behaviour as noted in section 4.5.5. Three candidates for conditions which may vary in the course of the measurements are:
1. Stress/stain in the MWNT (also effective probe size).
2. Mechanical instability in the junction geometry (e.g. thickness of polystyrene).
3. Disorder.

The sections below expands on these with the aim of finding an explanation which shows how one or possibly a combination of two or more could explain the behaviour observed experimentally.

5.1.2.1 Stress/Strain

Stress and strain affect the conduction properties of a nanotube via their interaction with the bonds, specifically how the $p$ orbitals are affected. It has been shown in a SWNT how bending mixes the $p$ and $sp^2$ orbitals, thus changing the electronic structure. More generally, though, unless the probes are moved deliberately, mechanical movement is drift induced and therefore continuous and gradual. Thus, any effect induced by stress or strain should be continuous and gradual. The exponents do not change in a continuous and gradual manner.

The effective probe size was also listed as a possible factor. As the probe size is a measure of the proximity of a metallic body, should the MWNT bend towards or away from the probe, the size and proximity of the metallic body as felt electrostatically by the MWNT changes. This effect can also be ruled out for similar reasons as stress or strain. In addition, if the effective probe size had a strong influence, a more dramatic correlation with the probe size would be expected.

Although bending in a plane is readily observed and measured, out of plane bends can only be detected via an adjustment of the focal plane in the SEM, giving little quantitative information. This means that there is a limit to the certainty to which stress/strain and the effective probe size can be measured.

5.1.2.2 Mechanical Instability

Mechanical instability within the junction results in a change in the precise electrostatic geometry; this was identified as the polymer thickness in Figure 5.1, which is actually an unnecessarily narrow view of mechanical instability.

For example, when making initial contact with a nanotube, the angle at which the nanotube strikes the probe (angle between the probe axis and MWNT axis) remains
the same even when the probe is moved (the contact point does not act like a pivot, rather it appears it is energetically favourable to increase the bend forced on the tube). However if the probe is moved enough, a sufficient bend is put into the MWNT and it will suddenly spring off completely or even break. If the probe is still close enough to the MWNT’s freestanding position, it may re-contact the probe at a different spot as seen experimentally in section 4.5.5.4. Thus, for gradual macroscopic movements the geometry of the microscopic junction will remain unchanged, or it will change completely, these radical changes are captured in Figure 4.26, p131 section 4.5.5.4.

An additional effect is the polymer coating on the nanotube, from the TEM images (Figure 4.4, Figure 4.5 and Figure 4.6) showing a coating along the whole tube, it is reasonable to presume that it would lie in-between the probe and the MWNT. Observed under electron bombardment of a TEM, the thickness of polystyrene coating appears to be unstable, with some consolidation in places, and thinning in others. A similar process may occur at the junction as the IV characteristic is measured.

If the high currents and/or voltages seen at the peak of the IV measurement cycle place the polystyrene layer under considerable stress, it is quite unlikely it would be perfectly stable. Precisely how the polymer thickness changes is difficult to say, if it is precipitated by a increases in the maximum voltage across and the maximum current through the junction then, this is done in steps, i.e. suddenly, matching the behaviour of the exponents. The stress the polymer is under and how it might be affected is examined in more detail shortly, section 5.1.3.1.

5.1.2.3 Disorder

Large currents could induce or possibly ‘heal’ disorder directly or indirectly by heating. But the body of literature on current carrying capacity of comparable MWNTs would suggest that at the current levels measured in this study, it is highly unlikely (~ 2 µA in the power law/offset ohmic regime). The same cannot be said for the thin layer of polystyrene. If a dynamic amount of disorder in the MWNT was responsible for the power law exponent we would expect a consistent trend in the exponent, increasing or decreasing, assuming the current consistently induced disorder (or healed disorder). In addition, to explain the exponent behaviour with disorder it would have to originate from a highly localised area at the junction.
Increasing disorder might decrease the exponent accounting for the general trend. Increases in the exponent would have to be accounted for by a change in the localised area of the junction, i.e. point 2 on p140. Therefore, if disorder was partially responsible points 2 and 3 could never be divorced.

5.1.3 Conclusions

We have discussed the possible dynamic conditions related to the nanotube and contact in very general terms, comparing the likely behaviour of the condition to the observed behaviour of the exponent. Throughout the analysis, there is the assumption that nothing significant takes place, and the quantities discussed are related in a linear manner i.e. it is assumed there are no threshold or step like relationships. In this simple analysis, instability in the precise geometry of the junction appears the most likely cause. It has a plausible relationship with observable quantities and changes in the polymer thickness are reasonable (see section 5.1.3.1 below). All that's been achieved thus far is to identify the possible causes of the unstable results, and, although the most probable cause has been identified, it remains speculative.

5.1.3.1 Stability of the Polystyrene

In the preceding sections, it was concluded that changes in the polystyrene thickness and or a change in the mechanical connection could account for the variation in exponent behaviour. This conclusion was based on the explanation's relative merits (i.e. this explanation matched the experimentally observed behaviour) rather than arguing that it was physically reasonable for the polystyrene to behave in this way. To investigate this polystyrene needs to be examined as a material in more detail.

Polystyrene is an amorphous polymer, with long polymer chains randomly organised. In this configuration, no molecular movement is possible. This gives polystyrene a brittle, glassy character below the glass transition temperature, T_g. Polystyrene has an exceptionally high T_g ~ 105 °C. Hence, the ease at which it could be cleaved at room temperature producing the hairy facture of exposed nanotubes. Above T_g the elastic modulus of amorphous polymers drops dramatically. They become rubbery. Previously brittle polymers are now flexible as long molecules and are able to move against each other. Polystyrene has no melting point, although at higher temperatures
the molecules can coil up further. Much of the background to polystyrene is obtained from Rosner (2001).

Considerable electrical and mechanical stress is placed on the polymer layer between the MWNT and the probe. A quick calculation shows electrical stresses in our case could be very severe indeed. For a 30 nm layer, just 0.6 V potential drop equates to the breakdown field found in ‘bulk’ polystyrene of 20 Vμm\(^{-1}\) (Asmatulu et al 2005 and references within). The breakdown strength of films of the order of 30 nm is rarely tested, and when an electron can tunnel this distance, ‘breakdown’ is even harder to define. The method of contacting a MWNT means it is always pulled (to some degree) in a direction normal to the SEM image plane, and the tension set-up within the MWNT means there will be mechanical forces acting on the MWNT-probe junction.

In addition to these conditions at the limits of a particular measurement, several micro Amperes of current are travelling through a very small cross-section of polystyrene. Given all this, it appears that \(T_g\) could be reached, and the polymer chains may exhibit some movement. Apart from the force of electrostatic attraction, bringing the nanotube and probe surface closer, a wetting of the probe by the polystyrene would also draw polymer chains from the closest point between the MWNT and the probe the edges. Asking the question, the other way round; is it likely the polystyrene layer could remain constant under these conditions? The conclusion is that most likely it cannot remain constant.

### 5.2 Luttinger Liquid

With regards to the energy scale of LL behavior it could be plausible for an LL state to exist in the MWNTs studied here, there has been several reports of the LL behavior extending to room temperature in SWNTs, e.g. Postma et al (2000). Although the current scale on which the power law is observed in our results is fairly consistent, up to \(~1\ \mu\text{A}\), the voltage scale is not. It can seem very large for a theory that describes the low energy excitations of charge in 1D. Yao et al (2000) experienced a similar phenomena with SWNTs, the fabrication sometimes yielded very high two terminal resistances, (presumed due to the contact resistance), a power law was seen at low energy for both high resistance and low resistance contacts, the exponents (\(\alpha \sim 0.65\)) are typical of a LL state in SWNTs. The currents up to which the power law was seen
are consistent; between the high resistance and low resistance contacts (the current scale is also consistent with the results in this thesis). However the voltage range was extended in the high contact resistance samples. In the same manner the high voltage scale sometimes seen in the results within Chapter 4 need not exclude a LL state.

In the absence of a parallel ground plane in our experiments, the LL length replaces the distance to the ground plane as the factor which controls the strength of the $e-e$ interactions. On average about 6 µm of the nanotube protrudes from the composite, although as much as 15 µm has been observed. Even taking this extreme value of 15 µm for length, only an exponent of $\alpha_{\text{end}} \sim 1.1$ is possible assuming the participation of only a single shell ($N = 4$). If a more realistic scenario corresponding to all metallic shells is considered ($N = 20$), the exponent drops to 0.56.

Larger exponents are possible, arising at the junction between two LLs. The larger exponents have been observed for both SWNTs and MWNTs (sections 3.7.1 and 3.9.3), end-to-end junctions produce the largest exponents, $\alpha_{\text{end-end}} = 2\alpha_{\text{end}} = 4\alpha_{\text{bulk}}$. Such junctions could be possible in this experiment if the MWNT was divided into two by a point of strong disorder. The exponent created by a junction between two LLs as described above (15 µm long, freestanding, $N = 4$), would still only be $\alpha_{\text{end-end}} \sim 2.2$. It is clear from Figure 4.27 that this is still below the average exponent observed.

Taking the most extreme cases to produce the largest exponents simply does not produce large enough exponents to explain the vast majority of the results. In any case these extreme cases are not really plausible. Going further and creating stronger interactions with longer screening lengths would still not produce exponents large enough. In the situations described above the screening length is already much larger than the nanotube radius, $l_g >> r_{\text{cnt}}$, therefore the term $\ln(l_g/r_{\text{cnt}})$ in equation (20) will change only slightly, giving only small increase in the exponent.

Calculation of the possible exponents has lead to the exclusion of a LL state on a quantitative basis, but a LL state can also be excluded on qualitative grounds too. Foremost amongst these is the cross over to an offset ohmic region, this is not predicted with LL theory. While LL theory would be in agreement with the experimental observations which put the power laws at MWNT-probe contact, it disagrees with the observation of a quite different, larger exponent when contacting the same MWNT further down (section 4.5.5.2, p127), LL theory would predict a
slightly smaller exponent. This is because the size of the exponent is determined by the bulk or collective state of the Luttinger liquid, and the probe being in a new place further down is not a dramatic change in the electrostatics as seen by a LL state within the MWNT.

5.3 An Alternative Explanation: Wigner Crystal

Power laws with large, non-universal exponent values have also been found in similar systems, but they are by no means equivalent to MWNTs. Two examples are summarised here.

Power laws have been observed in metallic NbSe₃ nanowires by Slot et al (2004). NbSe₃ nanowires are typically 30-300 nm and 2-20 µm long. The power law exponents found from the conductance temperature (GT) and the IV characteristics can vary significantly (on the same sample) $\alpha \sim 0.6 - 3$ from the GT measurements. The exponents from the IV measurements ranging to higher values, $> 4$. The power law is observed below 50 K, which was below the 2nd Peierls transition.

Power laws have also been observed by Aleshin et al (2004) in iodine doped polyacetylene ‘nano-fibres’ which consist of many polymer chains. The iodine dopant was introduced as polyacetylene is a semiconductor with a 1.5 eV band gap. However, the doping is expected to couple the 1D chains and introduce disorder, such that the “confinement effects are expected not to be significant.” The power law had similar features to that reported by Slot et al (2004), high exponents (2 – 7.2) differing for the IV measurement and the GT measurement, although it was observed in a different temperature range, $30 < T < 300$ K.

Both Slot et al (2004) and Aleshin et al (2004) ultimately concluded that the behaviour is unexplained. Although Slot et al (2004) concludes that some aspects of the results can be explained by EQF (with the behaviour located in the bulk and not the contact) and Aleshin et al (2004) concludes that some aspects of the results can be explained by LL-LL junctions (again not a phenomena occurring at the contact). Where the reports have common ground is that a 1D Wigner crystal is also able to explain some aspects of the results.

A 1D Wigner crystal is expected to give rise to power laws with non-universal exponents typically around 3 – 6 (Lee et al 2002). The form of exponent as given by
Lee et al (2002) means it cannot be less than one, precluding it from explaining the measurements of Slot et al (2004). A condition, which also precludes it from explaining the measurements in this thesis and those summarised in chapter 3.

Wigner crystals occur in solids with a low electronic density, which is why it is a possible explanation for the phenomena observed in a metallic nanowires (NbSe$_3$) which have undergone two Peierls transitions or a doped semiconductor (polyacetylene). It also why it is not something that is expected to be relevant for MWNTs.

The experimental evidence in both of these cases points to the power law originating from the nanowire or fibre bulk, not at the contact. This alone precludes the same explanation for the results presented in this thesis. In summary the physics at work in these systems is likely to be quite different to that in MWNTs in general, although it is likely to contain some similar ingredients.

5.4 An Alternative Explanation: Polystyrene Breakdown

Appendix 3 gives a detailed investigation into the possibility of a conduction mechanism within the polystyrene being responsible for the IV characteristic. The findings are summarised below.

There is only a single mechanism that has merit as a possible explanation, which is in the form of space charge limited conduction. Here, a power law is created from a distribution of trap sites below the 'conduction band'. Crucially though, within this picture the transition to offset ohmic needs to be regarded as a misinterpretation, as deviation from the power law is only possible when all the traps are filled and the more well known space-charge limited square law dominates, i.e. $I \propto V^2$ (not $V^3$). However, a $V^4$, offset ohmic dependence is clear in the data and cannot be mistaken for a $V^2$ dependence.

Quantitative analysis is difficult; many of the parameters involved can have wide variations. Despite this wide scope, many parameters need to be pushed to their extremes to obtain any kind of quantitative agreement. In addition, there is no qualitative agreement with previous reports on the conduction of polystyrene films.
5.5 Coulomb Blockade Theories

There are two single junction coulomb blockade based theories, EQF and EG. They differ in how the environment surrounding the junction is defined. EG theory (Egger and Gogolin, 2001), was developed specifically for disordered MWNTs. In both EQF and EG the tunnelling electron excites harmonic modes with a finite spectrum at low frequencies; this gives rise to the power law. The difference between EQF and EG, lies in how the environment is defined, and thus how the spectrum of the low frequency modes is computed. EQF takes a phenomenological approach defining the environment as a transmission line. EG follows a microscopic approach, defining the environment of disordered MWNT with parameters that take into account the level of disorder and e-e interaction strength. In EQF, the impedance of the transmission line is proportional to the power law exponent. In EG, the determination of the power law exponent is less straightforward, with numerical methods being necessary. Egger and Gogolin (2001) reported the exponent, $\alpha$ increases with disorder (smaller mean free path) and e-e interactions (larger interaction potential).

5.5.1 Environmental Quantum Fluctuations (EQF)

The nature of EQF theory already puts it in agreement with the observations indicating the power law originates from the contact, and is dependant on the specific properties of the contacts. Since the impedance probed is that of the immediate environment of the junction, changes in the polystyrene coating thickness and any change in location of the junction can unified by a single description; a changing electrostatic environment of the junction. It is this, together with the simplistic analysis presented in section 5.5.1.1 below that reproduces a critical element of the data in Figure 4.29 that makes EQF such an attractive proposition to obtain for a full explanation as given in section 5.5.1.3.

5.5.1.1 Linking Junction Capacitance and Impedance

The phenomenological approach in EQF theory relies on defining the junction environment with either lumped or distributed circuit components. A typical junction or array of junctions may be created by two overlapping metal strips, separated by an insulating layer, as shown in Figure 5.2. In this case, the strips or leads will have a
well defined (distributed) capacitance and inductance, based upon the geometry and possibly resistance (depending on the choice of material).

Figure 5.2: Schematic of overlapping metal strips (grey) separated by oxide (semi-transparent brown) forming a tunnel junction. The light blue indicating the volume which gives rise to the minimum junction capacitance. The size of the dark blue box is velocity dependant and gives an additional contribution to the junction capacitance.

The junction itself will have a well-defined capacitance based on the overlap area of the lead. This value of capacitance is only the minimum junction capacitance. There is a further contribution to the extracted junction capacitance from the distributed capacitance of the leads. This contribution is defined as:

\[ C = C_{\text{line}} \cdot d = C_{\text{line}} \cdot \tau_{\text{transit}} \cdot v \]  

(69)

It arises due to the finite tunnelling or traversal time, \( \tau_{\text{transit}} \). Environmental modes above the frequency, \( \tau_{\text{transit}}^{-1} \) are displaced adiabatically (rather than suddenly), and the distance travelled by these waves, \( d \) determines the size of the environment and hence contribution to the junction capacitance. \( v \) is wave velocity and \( C_{\text{line}} \) the capacitance of the leads, in Fm\(^{-1}\).

For the junction formed by a MWNT and probe, there is no well defined 'overlap capacitance', with all of the extracted junction capacitance arising from capacitance due to the environment-size, thus \( C_j = C \). As the line impedance, \( Z_{\text{line}} \) is strongly influenced by the line capacitance, \( C_{\text{line}} \) this leads to a much stronger relationship between the junction capacitance, \( C_j \) and the impedance, \( Z \). This is in contrast to conventional CB experiments (as shown in Figure 5.2), where \( C_j \) and \( Z \) can be relatively independent. In LL theory, the charge is transported by a single collective mode. This interacting Plasmon has a velocity:

\[ v = \frac{1}{\sqrt{L_{\text{line}} \cdot C_{\text{line}}}} = \frac{1}{C_{\text{line}} \cdot Z_{\text{line}}} \]  

(70)
More generally, equation (70) also describes the wave velocity on a EM transmission line. The junction capacitance can now expressed as:

\[ C_j = \frac{\tau_{\text{transit}}}{Z_{\text{line}}} \]  

(71)

If we assume the time \( \tau_{\text{transit}} \) to be constant, \( Z \propto C_j^{-1} \). Examining the data in Figure 4.29, this works quite well, although the negative intercept is not reproduced. The transit time can be extracted as either 1.1 or \( 1.4 \times 10^{-14} \) s from the slope in Figure 4.29. At first sight this value is a little on the large side for a tunnelling time, but it is still plausible.

There are however problems with this simple analysis. If \( Z_{\text{line}} \) is the extracted impedance, it makes \( \tau_{\text{transit}} = \tau_{\text{relax}} \), violating one of the inequalities BQF theory was developed with:

\[ \tau_{\text{transit}} < \tau_{\text{relax}} < \frac{eI}{I} \]  

(72)

A further problem is that to construct a plausible \( LC \) transmission line with a line impedance greater than 30 kΩ is impossible, and the line impedance at the junction is independent of the probe size, leaving no room to account for the possible probe size effect. There is also the assumption of a constant transit time to be discussed. Therefore, the extracted impedance appears to behave qualitatively like a line impedance, but quantitatively line impedances of the kind of values extracted from the results are impossible.

Another variation on this leads to similar conclusions, if the Fermi velocity, \( v_F \) is employed as velocity of charge on the line then equation (69) can be re-written as:

\[ C = C_{\text{line}} \cdot d = \frac{L_{\text{line}}}{Z_{\text{line}}} \cdot \tau_{\text{transit}} \cdot v_F \]  

(73)

This relationship gives, \( Z^2 \propto C_j^{-1} \) and does not work as well as \( Z \propto C_j^{-1} \), (71). But the fit still gives an \( R^2 \) value of 0.95. From this simple analysis, it appears that the extracted impedance behaves very much like an \( LC \) line impedance. The lack of a defined minimum \( C_j \) creates an intimate relationship between \( Z \) and \( C_j \) as they are both dependant on \( C_{\text{line}} \). However, as will become clear later in section 5.5.1.3, the impedances extracted from the experimental results are impossibly high.
5.5.1.2 Transit Time

In both attempts to link \( C_I \) with the line impedance it was assumed that the transit or tunnelling time was constant. Although ultimately the analysis in 5.5.1.1 was limited, the assumption of a constant tunnelling time is also made in section 5.5.1.3, and it is therefore essential to justify it, and quantify the tunnelling time.

In a review of the tunnelling time by Gasparian et al (2000), it is clear that the calculation of tunnelling time is not straightforward. However, one of results from the pioneering calculations of Hartman (1962) was that the transit time could indeed be constant. The tunnelling time was constant with barrier length for opaque barriers. The specification for an opaque barrier was made by Devort and Grabert (1992) as a condition for the observation of CB, where it was defined as \( R_T > R_K \), a definition that is possible if the junction area is microscopic. It is a condition easily fulfilled in our case, based on the values of \( R_T \) extracted in section 4.5.3. This definition based on tunnelling resistance rather than a resistivity, is not suitable for larger area junctions. Clearly whatever the barrier transparency, larger area junctions would produce smaller values of \( R_T \). Therefore, one should consider physically what shape and size of barrier is determined to be opaque enough, for \( \tau_{\text{transit}} \) to be constant. Gasparian et al (2000) concludes that a 1 eV barrier would have to be at least 1 – 2 nm long. Hartman (1962) calculated constant transit times for square barriers over 0.5 nm long (2.3 eV barrier height) and 0.3 nm (4 eV): A crude definition of the heightxwidth to be at least \( \sim 1.1 \text{ eVnm} \) would unite all these results.

All of these barriers could be considered short in comparison to the thickness of the polystyrene coating surrounding the MWNTs (~ 20 – 30 nm). Generally, barriers of this thickness or length are much less frequently used. Although Park et al (2004b) have used a 10 nm polystyrene tunnelling barrier to improve the external quantum efficiency of a polymer light emitting diode. Within the field of single charge tunnelling Ingold and Nazerov (1992) stated 10 - 100 nm thick tunnel barriers were under investigation at the time of writing.

Given the variety of calculation methods (at least seven), and shape of barriers, numerical results for transit time are varied. The review paper by Gasparian et al (2000) consistently gives \( \tau_{\text{transit}} \sim 10^{-15} \text{s} \), with respect to the metallic junctions used for single electron tunnelling phenomena. Examination of a references contained within
Gasprian et al (2000) serves to demonstrate the variation in transit times as shown in Table 5.1.

<table>
<thead>
<tr>
<th>$\tau_{\text{transit}}$ (s)</th>
<th>Barrier or Junction Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7 \times 10^{-14}$</td>
<td>Field Emission from metal</td>
<td>Buttiker and Landauer (1986)</td>
</tr>
<tr>
<td>$10^{14}$</td>
<td>Zener (inter-band tunnelling)</td>
<td></td>
</tr>
<tr>
<td>$1.3 \times 10^{-11}$</td>
<td>Josephson junction</td>
<td></td>
</tr>
<tr>
<td>$0.95 - 3.01 \times 10^{-16}$</td>
<td>Metal-vacuum-metal (square barrier)</td>
<td>Hartman (1962)</td>
</tr>
</tbody>
</table>

Table 5.1: Numerical Results for traversal time in several types of barrier or junction

With regard to the tunnel barrier of interest here, a ~ 30 nm polystyrene layer sandwiched between a MWNT and a Tungsten tip, tunnelling is indeed reasonable and has been observed on similar thickness films. The barrier encountered in this study is almost certainly classed as rather opaque and therefore $\tau_{\text{transit}}$ can be considered independent of thickness.

### 5.5.1.3 Modelling the Experiment

The kinetic inductance and quantum capacitance that makes up the nanotube transmission line are well defined and independent of anything external to the MWNT. They are re-defined here to include the number of modes:

\[
L_{\text{kin}} = \frac{h}{8 \cdot M \cdot v_p \cdot e^2} \tag{74}
\]

\[
C_2 = \frac{8 \cdot M \cdot e^2}{h \cdot v_p} \tag{75}
\]

However the electrostatic capacitance representing the $e-e$ interactions, is dependant on the geometry of conducting bodies surrounding the MWNT.

**Capacitance as a Function of Length**

For most MWNT conduction experiments performed on substrates the electrostatic capacitance can be defined as the capacitance (Fm$^{-1}$) of a wire suspended above a ground plane as given by Burke (2002):

\[
-151-
\]
\[ C_{es} = \frac{2 \cdot \pi \cdot \varepsilon}{\cosh^{-1}(2l_g/r_{cut})} \]  

(76)

In the on-substrate experiments, \( l_g \) the height above the ground plane is constant, along with the permittivity, \( \varepsilon \) and the nanotube radius, \( r_{cut} \). Therefore, the electrostatic capacitance \( C_{es} \) is also constant along the tube length. This is not the case for MWNT glancing a probe: The electrostatic capacitance is constantly changing along the length of the tube, which in terms of equation (76) can be thought of as a constantly changing \( l_g \). Indeed, this is how the electrostatic capacitance is calculated once several simplifications have been made, see appendix 2 for details. The calculation is based upon simplifying the MWNT glancing the probe to two metallic cylinders intersecting at right angles, as shown in Figure 5.3. The \( x \) axis is defined as the MWNT axis, with the origin at the point where the MWNT and the probe is closest.
Figure 5.3: (a) Simplified MWNT-Probe contact with axis superimposed. (b) Cross section defining the point of minimum separation at $x = 0$ and the separation at this point as $t_{poly}$.

The resulting line capacitance, $C_{ES}(x)$ is shown in Figure 5.4 for three values of polymer thickness. The logarithmic capacitance scale and the values of $t_{poly}$ chosen provide a good visual representation of how the form of equation (76) creates a strong variation in $C_{ES}(x=0)$ as $l_p \sim r_{cnt}$. Although not shown here, the effect on the probe size is to simply hasten the convergence of the various $C_{ES}(x)$ characteristics for
different values polymer of thickness, $t_{\text{poly}}$. $C_{ES}(0)$ and $C_{ES}(1 \, \mu\text{m})$ are broadly unaffected by the probe size. In addition, not shown is the effect of the MWNT radius. Given the form of equation (76), decreasing the MWNT radius has the same effect as an increase in polymer thickness.

Having calculated $C_{ES}$, we can now address the following queries:

1. How does the electrostatic capacitance, $C_{ES}$ compare with the quantum capacitance $C_Q$?

2. What size of environment would account for the extracted capacitance values?

In response to question 1, $C_Q$ depends on the number of modes and for the three different scenarios of a single shell ($M = 1$), all metallic shells ($M = 5$) and all shells ($M = 15$) quantum capacitances of 300, 1900 and 5800 aF/\mu m are obtained respectfully, making $C_Q$ significant for only the single shell case. To answer question two, if a typical value for the junction capacitance is, $C_J = 3 \times 10^{-19}$ F, (it's assumed $C_Q$ is not significant) and a 8 nm separation (dotted blue line in Figure 5.4), then the environment, $d$ would be $\sim 8$ nm. Which is relatively small for a junction environment, but waves on a MWNT transmission line have a velocity of $v_F = 8 \times 10^5$ ms$^{-1}$ or a slightly larger, enhanced velocity if the interacting plasmon velocity, $v$ ($v > v_F$) is used as in LL theory. Electromagnetic transmission lines will have a velocity which is some fraction of the speed of light, $3 \times 10^8$ ms$^{-1}$, creating much larger environments.
Figure 5.4: Electrostatic line capacitance along a 7 nm radius MWNT, \( C_{ES}(x) \), positioned above a 500nm radius probe, with the free space value for permittivity used. \( t_{pol} = 1 \) nm (solid red), 8 nm (doted blue) and 30nm (dashed green).

The simplifications made such that the capacitance can be calculated using equation (76) above are necessary in the absence of a complete 3D electrostatic simulation. Although such a simulation would provide an accurate \( C_{ES}(x) \), \( C_{ES}(x = 0) \) and \( C_{ES}(x > t_{probe}) \) are not affected by the simplifications and would therefore be identical. Consequently, so would the high and low frequency impedances \( (Z_{hf} \) and \( Z_{lf} \) shown later. The simplifications may have a minor effect on when the transition from one impedance value to another occurs. However, this is likely to be small relative to the effect of changing the probe size.

**Line Impedence as a Function of Distance**

Equipped with the result shown in Figure 5.4, the line impedance as a function of \( x \), \( Z(x) \) can now be calculated. The following factors all have an influence on \( Z(x) \): -
1. Number of modes $N$, which can also be described the number of participating shells $M$, where $N = 4M$.\

2. Probe radius.

3. MWNT radius.

4. Polymer thickness.

Given this, Figure 5.5 shows only a limited number of results, displaying the line impedance for various numbers of modes, or rather, participating shells. Factors 2 & 3 influence $Z(x)$ via $C_{ES}$, and their impact has been discussed previously.

Figure 5.5: Impedance along a MWNT. Probe radius 300 nm, tube radius 7 nm, polymer thickness 5 nm.

* Accurate only when the two lowest energy sub-bands are considered. If the Fermi level is sufficiently displaced, the number of modes could be $8M, 12M$ etc.
Input Impedance

Any impedance discontinuity, abrupt or gradual will produce reflections; the reflected waves change the ratio of voltage and current at the input, and therefore the impedance seen at the input. In the case of abrupt discontinuities, the reflections are readily calculated; making compensation for any such discontinuity that is imposed upon the designer of an RF circuit relatively easy. Two abrupt changes in the line impedance, one quarter wavelength apart constitute a \( \frac{1}{4} \) wave transformer. Provided the impedance of the \( \frac{1}{4} \) wavelength section is chosen correctly, the reflections produced will cancel, providing an undetectable transition from the line impedance at the input and to the line impedance of the output. Although a gradual transition may provide a better broadband response than a \( \frac{1}{4} \) wave transformer, they are rarely introduced deliberately. Given a specified reflection coefficient the synthesis of a suitable, (if not ideal) \( Z(x) \) is possible. Should a particular transition shape be forced, the challenge is usually calculating the \( Z(x) \) characteristic given the disruption to the EM wave, an exercise that also yields the reflection. So the problem of having a known \( Z(x) \) and calculating the reflection coefficient is not a common one in RF engineering.

A crude approximation for the voltage reflection coefficient when reflections are small is given in Kraus and Fleisch (1999):

\[
\rho_v = \frac{\Delta Z}{Z} \tag{77}
\]

Using this approximation, Figure 5.6 shows the calculated input impedance. The x-axis scale shows the wavelength relative to the length of impedance transition.
Figure 5.6: Input impedance calculated using equation (77). $M = 5$, tube radius 7 nm probe radius 500 nm, polymer thickness 20 nm. The transition length simulated was 10μm.

This approximation is inadequate in this circumstance as the reflection coefficient is large, ($> 0.1$), giving input impedances at long wavelengths ($> 16$ kΩ) that are larger that the termination impedance, $Z(x_{\text{max}})$ ($\sim 10$ kΩ). The inadequacy of the approximation stems from its failure to account for multiple reflections. This result is of some value, as it shows the general shape of $Z_{\text{in}}(\lambda)$. At long wavelengths reflections add constructively to produce a large input impedance which should be equal to the termination resistance. In this case as in all simulation results presented here the line has, been terminated such that no reflections are produced at termination, i.e. $Z_{\text{load}} = Z(x_{\text{max}})$, i.e. a semi-infinite transmission line is simulated.

Where the transition length is of the order of the wavelength, the reflections begin to add destructively back at the input, reducing the input impedance. A shoulder in the slope is produced where once again reflections add constructively having travelled just over a wavelength. The same effect explains the ripples as $\lambda$ reduces further towards the point where there is a negligible net reflection, and the input impedance is given by the line impedance at the transition start, $Z_{\text{in}} = Z(x = 0)$. The exact equation
for the reflections generated form a gradual change in line impedance is given in Collin (1992):

\[ \frac{d\Gamma}{dx} = 2 \cdot j \cdot \beta \cdot \Gamma - \frac{1}{2} (1 - \Gamma^2) \frac{d^2(\ln Z_{\text{line}})}{dx^2} \]  

Equation (78) is a Raccati equation, and non-linear due to the $1 - \Gamma^2$ term. It does not have a known general solution. Rather than attempt a solution of equation (78) for the $Z(x)$ determined previously in Figure 5.5, a finite element simulation was performed with HPeesoft ADS, a package designed for RF and microwave circuit simulation. The MWNT impedance transition over 5μm was simulated using 400 elements of ideal transmission line, and terminated such that no reflections are produced.

![Figure 5.7: Real part of the simulated $Z_{\text{in}}(\omega)$ (solid lines) and analytical fit to simulation results (dotted lines). Two polymer thickness green = 30 nm red = 2 nm.](image)

Figure 5.7 and Figure 5.8 show the simulation results for the real part of the input impedance in solid lines. Using only 400 elements leads to inaccuracies as the electrical length of each segment tends to the excitation wavelength and spurious resonances are produced thereafter. Although the calculated results shown in Figure 5.6 were also calculated based on finite segment lengths, this number could be chosen arbitrary and was greater than 400. Therefore, with comparison to Figure 5.6, it is possible to judge what features are genuine and which ones arise due to the finite number of transmission line elements. The shoulder seen approximately half way down the slope is common to both results and should be considered a genuine attribute of $Z_{\text{in}}(\omega)$. The spikes after 100 THz are not genuine. Although a considerable increase in the number of elements would produce a more elegant result, it is not
necessary as the behaviour of $Z_{in}(\omega)$ is well known in the frequency limits ($Z_{in}(\omega \to 0) = Z_{load}$, $Z_{in}(\omega \to \infty) = Z_{line}(\lambda = 0)$). The purpose of the simulations is to determine the location of the roll-off from the low frequency limit to the high frequency limit.

![Figure 5.8](image)

Figure 5.8: Real part of the simulated $Z_{in}(\omega)$ (solid lines) and analytical fit to simulation results (dotted lines). Change in probe size, orange 200 nm probe, blue 800 nm probe radius.

In order to get the numerically calculated $Z_{in}(\omega)$ into analytical form it is fitted to a simple expression for the input impedance. In Figure 5.7 and Figure 5.8, these fits are shown by a dotted line. The fit was made manually, with the focus on replicating the initial roll-off. The approximation is made up by a frequency independent impedance $Z_{hf}$ in series with another impedance which effectively becomes shorted at high frequencies. An equivalent circuit representation is shown in Figure 5.9.

![Figure 5.9](image)

Figure 5.9: Circuit representation of input impedance approximation.
The analytical form of the $Z_m(\omega)$ approximation is given in Equation (79) where the capacitor, $C_j$ in Figure 5.9 has been expressed in terms of a frequency, $f_{3dB}$.

$$Z_m(\omega) = \frac{1}{(Z_y - Z_{0f})^{-1} + \left(\frac{i \cdot \omega}{2 \cdot \pi \cdot f_{3dB} \cdot (Z_y - Z_{0f})}\right) + Z_{0f}}$$  \hspace{1cm} (79)

At this point it should be noted that frequency $f_{3dB}$ in Equation (79) will always be slightly less than the measured 3 dB point of the function $Z_m(\omega)$, and the simulated $Z_m(\omega)$.

**Charge Decay on Junction Capacitor**

With the analytical input impedance given by Equation (79), it is possible to find the charge or voltage decay function $R(t)$ by an inverse Fourier transform. If one considers a charged capacitor connected to a simple resistor, the charge will decay exponentially. This exponential is a result of the inverse Fourier transform of the total impedance as seen by the voltage on the capacitor, which is the capacitor's reactance in parallel with the resistor. The total impedance seen by the junction is $C_j$ in parallel with $Z_m(\omega)$. As for $C_j$ to reach equilibrium with the bias, it needs to discharge through $Z_m(\omega)$. Equation (80) shows the inverse Fourier of the total impedance, $Z_m(\omega)$ in parallel with $C_j$. It is multiplied by the junction capacitance to give the charge decay function as in Ingold and Nazarov (1992).

$$R(t) = \frac{1}{2 \cdot \pi} \int_0^\infty \frac{C_j}{Z_m(\omega) + j \cdot \omega \cdot C_j} \cdot \exp(j \omega t) \cdot d\omega$$  \hspace{1cm} (80)

After integration, and reduction for the real part is given by:

$$R(t) = \frac{(B + A - 1) \cdot \exp^2 \frac{-1 \cdot 1 + B - A}{2 \cdot C_j Z_{0f}} + (A + 1 - B) \cdot \exp^2 \frac{-1 \cdot 1 + B + A}{2 \cdot C_j Z_{0f}}}{4 \cdot A}$$  \hspace{1cm} (81)

$$B = 2 \cdot C_j \cdot \pi \cdot f_{3dB} \cdot Z_y$$

$$A = \sqrt{1 + 2 \cdot B + B^2 - 8 \cdot C_j \cdot \pi \cdot f_{3dB} \cdot Z_{0f}}$$

Equation (81) describes the real part of the charge relaxation function, as the sum of two exponential decays, with different amplitudes. The first exponential term is a fast decay with a time constant $\sim C_j Z_{0f}$ and the second exponential term is slow decay,
with a time constant \( > C_jZ_f \) (at least for typical combinations of values used here). Defining the extracted impedance as a function of junction capacitance and the relaxation time:

\[
Z_{\text{extracted}} = \frac{\tau_{\text{relax}}}{C_j}
\]  

(82)

With the relaxation time given by the slow exponential:

\[
\tau_{\text{relax}} = \frac{2 \cdot C_j \cdot Z_{hf}}{1 + B - A}
\]  

(83)

Given that \( \tau_{\text{relax}} > Z_fC_j \), large values for the extracted impedance result from perfectly plausible line impedance values. Before proceeding to a comparison of the extracted impedances and junction capacitance, there are a couple of issues to covered. Examining Figure 5.8 and Figure 5.7, \( f_{3dB} \) is not constant with tip size or polymer thickness. These two effects can be considered independent as long as \( t_{\text{poly}} < r_{\text{probe}} \).

Also, the use of the slow exponential needs to be justified. Equation (81) does not change with \( f_{3dB} \), but intuitively the relative importance of the exponentials should shift with the location of \( f_{3dB} \) relative to the roll-off created by the reactance of \( C_j \).

**Figure 5.10**: \( f_{3dB} \) dependence on polymer thickness, \( t_{\text{poly}} \). The simulation conditions were, \( r_{\text{cat}} = 7\text{nm}, r_{\text{probe}} = 500\text{nm} \). The symbols represent different numbers of participating shells; black cross - metallic shells \((M = 5)\), red circles - single shell \((M = 1)\), green triangles - all shells \((M = 15)\). The dotted line shows the data fit.
Figure 5.10 shows $f_{3db}$ to have a dependency on the polymer thickness, $t_{poly}$. $f_{3db}$ plotted against $Z_{hf}$, which is a function of $t_{poly}$ gives a linear relationship. The trend in Figure 5.10 has its root in the impedance definition, and it is therefore fitted with an equation of the form of the $C_{ES}^{-1}$ (equation (76)). This fit is more versatile than one based on $Z_{hf}$, which would have an additional dependency on the number of participating shells.

Unlike the $f_{3db}$ dependence on polymer thickness, there is no obvious analytical form for the relationship between $f_{3db}$ and $r_{probe}$ shown in Figure 5.11. Equation (84) provides the fit shown in Figure 5.11, with $R^2$ value $> 0.99$. With a good fit, the exact form of equation (84) is not important, as long as the values of $r_{probe}$ remains within the limits of those simulated.

$$f_{3db}(r_{probe}) = A_2 + \frac{A_1-A_2}{1+(r_{probe}/x_0)^p}$$

(84)

Where $A_1, A_2, x_0$ and $p$ are constants.

Figure 5.12 shows what could be two input impedances as defined in equation (79), with different roll off or $f_{3db}$ frequencies. At what input impedance the green line of the junction reactance, $X_c$ intercepts $Z_{in}(\omega)$ decides what impedance will dominate the
relaxation time. If \( f_{\text{intersec}} \) is defined as the frequency at which \( Z_{\text{in}}(\omega) \) and \( X_c \) intersect, then:

\[
\begin{align*}
  f_{\text{intersec}} > f_{3dB} & \quad \tau_{\text{relax}} = C_j \times Z_{hf} \\
  f_{\text{intersec}} < f_{3dB} & \quad \tau_{\text{relax}} = C_j \times Z_{lf}
\end{align*}
\]

Figure 5.12 also serves to illustrate one of the trade offs confronting those seeking to observe a single junction CB within EM environments. Resistive materials and the geometry of the leads could influence \( Z_{hf} \) and \( f_{3dB} \). But, unless \( C_j \) was large it is difficult to move the green reactance line far enough left to intersect \( Z_{hf} \), rather than \( Z_{lf} \). Increasing \( C_j \) imposes the need for lower and lower temperatures, eventually making it impractical.

![Figure 5.12: input or line impedance characteristics and intersection with junction reactance.](image)

Equation (81) is dissected in Figure 5.13, showing that for high values of \( f_{3dB} \) relative to \( C_j \) (as shown by the red line in Figure 5.12) the amplitude of the slow exponential (also red in Figure 5.13) dominates. In this regime \( f_{3dB} \) has an independent time constant \( \tau_{\text{relax}} = Zlf \times C_j \). For low values of \( f_{3dB} \) the fast exponential dominates with \( \tau_{\text{relax}} = Z_{hf} \times C_j \). However, it is the region in the middle where the roll off of \( Z_{\text{in}}(\omega) \) and the intersection with \( X_c \) occur at approximately the same frequency, which is of interest. In this regime the slow exponential has a time constant even longer than \( Z_{lf} \times \)
$C_J$ and the fast exponential a time constant even shorter than $\frac{Z_0}{C_J}$. Neither exponential can be considered to dominate over the other. As long as the slow exponential is not negligible it will hold a strong influence over the extracted impedance.
Figure 5.13: Parts of Equation (81) time constants of the two exponentials and their amplitudes as $f_{sub}$ changes. $C_f = 1.7 \times 10^{-19}$ F, $Z_{gf} = 10,212 \, \Omega$, $Z_{hf} = 4,198 \, \Omega$ (Based on $M = 5$ and a $t_{pol} = 5 \, \text{nm}$).
Reproducing the Impedance and Capacitance Relationship

Returning to Figure 4.29, it has been postulated that the variation in the results is caused by the difference in the precise electrostatic geometry of the junction, excluding a change of the junction location. It is the changes in polymer thickness that should be responsible for the pattern seen in Figure 4.29. \( C_J \) is primarily defined as a function of \( \tau_{\text{transit}} \) and \( t_{\text{poly}} \), see equations (69) or (73), noting that \( C_{\text{line}} \) is dependant on the polymer thickness. The extracted impedance is defined by equation (82), and it is also strongly influenced by \( t_{\text{poly}} \). The polymer thickness is assumed to vary, and all the other influences over \( C_J \) and \( Z_{\text{extracted}} \) (\( \tau_{\text{transit}}, t_{\text{probe}} \) and \( M \) the number of participating shells) are constant. Their values are chosen to produce the best fit, with the experimental results together with a range of \( t_{\text{poly}} \) values. The best fits are shown in Figure 5.14.
Figure 5.14: Theory and experiment, with two fits. The experimental results are shown as before in Figure 4.29. Filled blue circles for the capacitance values extracted from the low voltage offset ohmic fits, and the red open square is the data point where only one offset ohmic fit was present. Shown in dark and light grey are straight line data fits for 4-point and 5-point based fits respectively (also as in Figure 4.29). The fits produced by the theory are shown in orange and solid dark yellow. With plus signs showing calculations for all metallic shells participating, \( M = 6 \) with the polymer thickness varying between 0.5 nm and 25.5 nm, in 1 nm steps. The full set of parameters is shown in the red row of Table 5.2.

The good match between the calculated result and the experimental data shown in Figure 5.14 is quite robust. All the parameters, \( M \), \( t_{\text{poly}} \) range, \( \tau_{\text{transit}} \) and \( r_{\text{probe}} \) can be adjusted by ±30% but due to the robust fit obtained, the features of the curve remain the same, i.e. tending to linear with larger \( Z \), with gradients and intercepts of a similar order.

The transit time and range in polymer thickness can be traded off against one another. A reduced transit time can be compensated for extending the range in polymer thickness. This is simply moving the intersection of \( Z_{\text{in}}(\omega) \) and \( X_{\text{c}}(\omega) \), with the transit time influencing \( C_j \), and \( t_{\text{poly}} \) influencing \( f_{3\text{db}} \) (Figure 5.10).

The fit shown in Figure 5.14 was obtained by increasing the probe radius from 500 nm to 900 nm, this is in effect reducing \( f_{3\text{db}} \) from 20 THz to 18 THz. Given the error
in measuring the probe size due to the poor SEM resolution and many, but individually justified simplifications in the modelling of a MWNT glancing the probe, this kind of adjustment in \( f_{3db} \) is very small, and quite reasonable.

With many modes, lower impedances are possible. However, with reference to Figure 4.27, there are only two impedances below 20 kΩ. Therefore, the fact that a good fit down to an impedance \(~10\, \text{kΩ}\) is not possible with ‘average’ circumstances does not rule out the all-metallic layers participating case. A large, many layered tube with a few more than the average of 1 in 3 layers being metallic is quite plausible, a calculation with \( M = 15 \) is shown in green in Figure 5.15, which does offer an improved fit to the low impedance data points.

![Figure 5.15: Theory vs. experiment for several modes detailed in Table 5.2. Cyan - single shell, Red - metallic, Green - All shells. Blue - \( M = 200 \). Solid navy blue circles are the experimentally extracted values, with \( C_J \) obtained from the lower segment of the offset ohmic regime. The open red square is the point where it was only possible to extract one value for \( C_J \). Dark grey line is the 4 point fit to experimental data (blue circles).](image)

\( A_{long} \) is defined as the amplitude of the slow exponential in Equation (81) i.e.: -

\[
A_{long} = \frac{B-1+A}{4A} \tag{85}
\]

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Discussion of Conduction Results

<table>
<thead>
<tr>
<th>Theory fit</th>
<th>Shells, M</th>
<th>( r_{probe} ) (nm)</th>
<th>( \tau_{transit} ) (s)</th>
<th>( t_{poly} ) range (nm)</th>
<th>( A_{long} ) range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyan</td>
<td>1</td>
<td>600</td>
<td>( 8.0 \times 10^{-15} )</td>
<td>0.5 - 20.5</td>
<td>0.36 - 0.11</td>
</tr>
<tr>
<td>Red</td>
<td>6</td>
<td>900</td>
<td>( 8.0 \times 10^{-15} )</td>
<td>0.5 - 25.5</td>
<td>0.26 - 0.04</td>
</tr>
<tr>
<td>Green</td>
<td>15</td>
<td>1200</td>
<td>( 8.0 \times 10^{-15} )</td>
<td>0.5 - 25.5</td>
<td>0.20 - 0.02</td>
</tr>
<tr>
<td>Blue</td>
<td>200</td>
<td>1500</td>
<td>( 8.0 \times 10^{-15} )</td>
<td>0.5 - 22.5</td>
<td>0.07 - 0.006</td>
</tr>
</tbody>
</table>

Table 5.2: Parameter sets for calculating results shown in Figure 5.14 and Figure 5.15.

Possibly the best match to the data in Figure 5.15 was obtained based on \( M = 200 \), shown in blue, demonstrating for the larger number of modes the best match is obtained at the lowest impedance. For 200 shells (800 modes), the transmission line could be considered to be in the electromagnetic (EM) region, with line impedances around 377 \( \Omega \). Given this, it does not appear correct that such large impedances could have an EM origin. The re-examination of the question how reasonable it is to use the slow exponential as the relaxation time holds the answer. The amplitude of the slow exponential is negligible relative to the fast one. The use of the slow exponential to define \( \tau_{relax} \) is not justified.

No set of parameters was found which enabled a single shell to show a good fit with the experimental data. The maximum amplitude for either exponential curve is 0.5. With this in mind, it can be said that the slow exponential plays a role in the charge decay function, \( R(t) \), for \( M = 1-15 \). As Table 5.2 shows, \( A_{long} << 0.5 \) for the \( M = 200 \) case.

In conclusion, the model successfully explains the measurements using realistic parameters:

- The polymer thickness used are those observed in TEM.
- The transit time is right in the middle of the acceptable range (Gasparian et al 2000).
- Probe size is slightly different compared to the almost perfect agreement of \( t_{poly} \) and \( \tau_{transit} \). But not very different and is within errors created by the simplifications in calculating \( C_{lin}(x) \).  

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• The number of modes correlates well with other studies (Tarkiainen et al 2001) and theory. It is difficult to justify $M = 1$ and $M > 15$ (as the typical value) for various reasons.

**Nanotube LC Transmission Line**

There is no direct evidence for ballistic or non-ballistic transport in our MWNTs. There is only evidence for a 1D electronic structure guaranteeing $l > 2\pi r_{\text{crit}}$. It could be said that there are then two valid points of view:

- Transport in the metallic sub-bands is ballistic, so the LC model is correct, or
- Transport is not ballistic and a resistive component should be added to form an $LCR$ transmission line

**Option 1: The LC Model**

From the literature review it should be clear that transport in MWNTs at room temperature can be ballistic over at least 1.4 $\mu$m (Urbina et al 2003 and Poncharal et al 2002). Strictly speaking it is ballistic only in the metallic bands. This is due to two factors. The different manner in which semiconducting and metallic sub-bands couple to long range disorder (McEuen et al 1999), and, the circumferential disorder averaging is very effective with the large diameter of MWNT shells (White and Todorov 1998).

Those who have observed a power law and considered whether a MWNT should be modelled as a $LC$ or $LCR$ transmission line have always decided it should be an $LC$ transmission line. Tarkianen et al (2001) justified it simply because it worked well. Bachtold et al (2001) used it because the resistive component was not significant at the relevant frequencies. In both cases, they were modelled as many mode ($N > 4$) transmission lines. In Tarkianen et al (2001) the many modes originated from the capacitive coupling of metallic shells. Bachtold et al (2001) presumed that the Fermi level was positioned such that many sub-bands of different character were participating. Tarkianen et al (2001) described capacitive coupling of all metallic shells was due to the low frequency AC method of measurement. Although in the CB description one would naturally expect the shells to be coupled even with a DC measurement. As the arrival of a tunnelling electron excites waves down the transmission line. Bachtold et al (2001) and Tarkianen et al (2001) have arrived at
identical mathematical descriptions of an LC transmission line, although the physical origin is slightly different.

According to the theoretical predictions of single junction CB, the observation of a power law means the transmission line is lossless (LC). Resistive transmission lines do produce a strong zero bias anomaly but it is not characterised by a power law. It’s form is given by equation (49) (Flensberg et al 1992).

**Option 2: LCR Model**

Bachtold et al (2001) sought to investigate how significant the series resistance was. With the measured resistance of for MWNTs ~ 5 kΩ/μm, it was found to be equal to the series inductance in the transmission line at frequencies corresponding to 3 meV and since the power law extended beyond this voltage the LC model is appropriate.

Without a direct measure of the MWNT resistance in our case, we will work backwards, considering the resistance necessary to influence the extracted impedance. Which is to say; what value resistance will be significant compared to the inductance at the frequencies around 10 THz (~ $10^{13}$), where $C_f$ shorts out the environmental impedance. A MWNT transmission line with 5 metallic shells participating has an inductance of ~800 pH/μm. For an equal resistive component at $10^{13}$ Hz the total series resistance should be ~ 50 kΩ/μm. Taken per shell, that gives a resistive component in each shell of ~ 250 kΩ/μm. Are such resistances likely?

<table>
<thead>
<tr>
<th>Resistance</th>
<th>Conditions etc.</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 to 25 kΩ/μm</td>
<td>Outer shell only</td>
<td>Bourlon et al (2004)</td>
</tr>
<tr>
<td>10 kΩ/μm</td>
<td>EFM measurements</td>
<td>Bachtold et al (2000)</td>
</tr>
<tr>
<td>5 to10 kΩ/μm</td>
<td>Two terminal measurements</td>
<td>Bachtold et al (2001)</td>
</tr>
<tr>
<td>4 kΩ/μm</td>
<td>Four probe measurements</td>
<td>Schönenberger et al (1999)</td>
</tr>
</tbody>
</table>

Table 5.3: MWNT resistances found in the literature.

From Table 5.3 it is clear that such a resistance (both cases total resistance, 50 kΩ/μm or per shell, 250 kΩ/μm) is not consistent with the measurement resistances of comparable MWNTs.
In conclusion, the LC model is appropriate for this purpose even if the MWNTs are not considered ballistic conductors as the resistance required to make a significant difference would be out of the range of resistances typically found for MWNTs.

**Limits of the Model**

Polystyrene has a relative permittivity of 2.5 (e.g. park et al 2004b). However, all the calculations were based on the permittivity of vacuum i.e. a relative permittivity of 1. If the permittivity of polystyrene is constant in the relevant frequency range 0 to ~ 1 PHz, then \( C_{\text{lin}}(x \to 0) \) will be slightly larger, and the effect of this would be to slightly increase the range of values for \( t_{\text{poly}} \) or reduce the value of \( \tau_{\text{trans}} \) needed to produce the good agreement with measurements. The high frequency impedances would be slightly lower. In conclusion, the effect of incorporating this inharmonious permittivity into the calculations would not prevent or significantly change the ability of the theory to provide a good match to the experimental results using a reasonable parameter set.

The approximation of \( Z_{\text{sp}}(\phi) \) is another source of error in the calculations. With the fit focused on replicating the initial roll-off from \( Z_{\text{fr}} \), additional pairs of capacitor and impedances, in parallel with each other could be placed in series with the circuit shown in Figure 5.9 to replicate features like the shoulder seen on the slope between \( Z_{\text{fr}} \) and \( Z_{\text{sp}} \) (Figure 5.7 and Figure 5.8). This would of course significantly complicate the charge relaxation function \( R(t) \), equation (81), adding more exponentials.

It could be argued that the fit should be in the middle of the decay, i.e. overestimating \( Z_{\text{fr}} \) at the initial roll-off, instead of fitting to the initial roll off and underestimating \( Z_{\text{fr}} \) for all frequencies thereafter. Apart from the overestimating, the fit is much harder to judge manually (the spurious results of the simulation at high frequencies preclude the use of simple automated fits). Such a fit would increase \( f_{\text{str}} \), slightly and may adversely effect the good agreement between experiment and theory.

All of the above are essentially complications which were justifiably left out earlier. When examining their probable effect it leads one to the conclusion that they do not significantly affect the good fit achieved between experiment and theory and could possibly offer marginal improvements on this agreement.
5.5.2 Egger and Gogolin Theory (EG)

In the case of EG, the numerical calculations in Egger and Gogolin (2001), reproduced exponents typically seen in on-substrate configurations, e.g. $\alpha \sim 0.3$ and for certain parameter sets, values of $\alpha \sim 2$. A large exponent would require a strong degree of disorder, strong e-e interactions or a mixture of both. The undoped arc-discharge MWNTs used here are expected to have a high degree of structural perfection (confirmed by our TEM), leaving only a small degree of disorder, intrinsically present in MWNTs due to inconsummate adjacent shells. There is also strong evidence from the IV measurements, Section 4.4, that supports this presumption. The analysis shows that the conductivity is dependant on the 1-D DOS. Additionally, disorder as the dominant contribution to the exponent does not sit well with the experimental observations. There would have to be a large variation in disorder from tube to tube (there is no reason to suggest that disorder would be unevenly distributed) and the same variation of disorder would have to occur during the experiment. As stronger disorder increases the exponent, the current would have to reduce the disorder significantly to account for the changes in the exponent.

It therefore falls upon the interaction strength to account for the large exponents, and the variation in the exponent. The e-e interactions would have to be very strong. It is not clear if all this can be achieved by an interaction potential definition that could also replicate the observed decreases in exponent, with the polystyrene thickness decrease, or if the relationship in Figure 4.29, p135 would be replicated too. If the definition is similar to that of LL theory, i.e. it derives from the electrostatic capacitance of a wire above a ground plane, then the requirements of being sensitive to the small changes in polymer thickness and the requirement of strong interaction are conflicting.

5.5.2.1 As Applied in Kanda et al (2004) and Bachtold et al (2001)

Kanda et al (2004) applied EG’s theory based upon $l \leq 2\pi r_{ct}$ and Bachtold et al (2001) applied it based upon $l \geq 2\pi r_{ct}$. In both cases the exponent was given by:

$$\alpha_{bulk} = \frac{r_{ct}}{2 \cdot \pi \cdot \hbar \cdot D \cdot v_0} \cdot \log(1 + v_0 \cdot U_0)$$

(86)

Where:
Paul Smith  

Discussion of Conduction Results

- $v_0$ is the non-interacting DOS. Given by:

$$v_0 = \frac{M}{2 \cdot \pi \cdot h \cdot v_F} \quad (87)$$

- $U_0$ is the effective short ranged 1D interaction potential which is not the same as $U$ in section 3.8.4, equation (53).

- $D$ is the diffusion constant, approximated by $D \approx v_F l$.

Kanda et al (2004) approximates later factors of equation (86) to $\sim 1$, while Bachtold et al (2001) approximates it to $\sim 2 - 3$. The two authors arrive at equivalent expressions for the exponent:

$$\alpha_{\text{bulk}} = \frac{r_{\text{ext}}}{l \cdot M} \quad (58)$$


$$\alpha_{\text{bulk}} = \frac{20 \cdot r_{\text{ext}}}{N \cdot l_e} \approx \frac{20 \cdot r_{\text{ext}} \cdot R^*}{R_K} \quad (56)$$


Table 5.4 shows the assumptions made for the free path and the number of modes, $N$ which determines the exponent calculated from EG theory. Bachtold et al (2001) uses more modes, and free paths greater than circumference as there was evidence for this. The range of calculated exponent values are small compared to those found experimentally. Bachtold et al (2001) concluded EG’s theory could not explain the results.

Kanda et al (2004) uses fewer modes, corresponding to 2.5 metallic shells or 1 shell where one considered the MWNT to be doped and semiconducting bands to be participating. In order to get exponents closer to the experimentally observed values the free path values are around the size of the circumference or less. Kanda et al (2004) concluded EG’s theory could explain the experimental results as the calculated exponents are in the range of those found experimentally.
### Table 5.4: Calculated exponents using EG theory as applied by Kanda et al (2004) and Bachtold et al (2001).

With evidence for the 1D structure of the MWNTs studied here, the mean free path will be greater than the circumference, similar to Bachtold et al (2001), EG theory in this circumstance produces exponents almost two orders of magnitude smaller than those observed in our results. Therefore EG theory in the 2D limit, (i.e. the regime in which the exponent can be determined analytically) cannot explain the results presented in this thesis.
6 Conclusions

There is without doubt convincing evidence for ballistic conduction in MWNTs at room temperature over distances of ~1.5 μm. Equally, there are many examples of diffusive conduction in MWNTs, over similar or shorter distances. Ballistic conduction is not restricted to the crossing sub-bands. SWNT-FETs are generally accepted to be ballistic at room temperature, when the channel length is below 300 nm.

Claims of ballistic conductance over lengths around ~1.5 μm in metallic sub-bands of MWNTs are not particularly at odds with all other experiments or theory. The impact of disorder is considerably suppressed in the metallic bands of the large diameter MWNTs (that is relative to the diameter of SWNTs). This leaves phonons as a possible source of backscattering. Only acoustic phonons are relevant for low bias, and there is a spread of calculated and experimentally extracted mean free paths due to acoustic phonons, ranging from a few hundred nm upwards, beyond 1.5 μm.

The convincing evidence for both ballistic and diffusive conduction in MWNTs has moved the debate on to what experimental conditions might give rise to diffusive behaviour. Within this debate surfactants are a prominent issue, and a definitive outcome has not yet been reached.

It is however not necessary to assign the MWNTs to be ballistic or diffusive conductors for the EQF interpretation to be applied in this thesis. Just as exact nature of conduction in the MWNTs studied here does not impact upon the interpretation given nor does the issue of doping. Present in Chapter 3, though not specifically addressed, was the favoured ‘p-type’ behaviour of carbon nanotubes. This behaviour appears to be due to the physisorption of oxygen (e.g. inner shells of the MWNT appeared perfectly ambipolar). The explanation proposed for the original results
presented in this thesis, models a MWNT transmission line consisting of all the metallic sub-bands capacitively coupled. Within this picture, the issue of whether the Fermi level is slightly adrift from the charge neutrality point (in the outer shells or indeed all shells) is not relevant. Even if it is so far adrift as to result in degenerate semiconducting sub-bands, these sub-bands are effectively seen as ‘short circuited’ by metallic sub-bands.

A weakness of the unconventional freestanding geometry is that it is not capable cooling the sample, which allows for the conductance-temperature characteristics to be determined. In terms of presenting convincing evidence for a power law, this is countered by the results presented in Chapter 4, where the $IV$ is shown to follow a power law over five orders of magnitude. This range is at least two orders of magnitude larger than the best offered in Chapter 3. One reason for this stems from the relative cost (time and money) of sample preparation for conventional on-substrate methods. The freedom to risk sample destruction extends the range at the upper boundary, while an excellent measurement set-up extends at the lower end.

The offset ohmic characteristics are also remarkably good. Figure 4.19 closely resembling the theoretical results of Girvin et al (1990). This is all without accounting for the distortion of the tunnel barrier at high voltage, a correction often employed when interpreting single junction CB experiments. Although the need for such a correction can be seen in some measurements when $eV > E_C$.

With such large power law exponents, it is clear that Luttinger liquid (LL) theory would never be able to account for the $IV$ measurements, even when considering the power law regime in isolation. Moreover, LL theory does not fit with many of the other experimental observations.

Unlike LL theory, Egger and Gogolin (EG) theory is not so amenable to a direct, quantitative comparison with experiments. The uncertainty surrounding the interaction strength definition and lack of an analytical expression for the exponent makes EG theory impossible to rule in or out definitively. However, it is possible to say that from the high power results the, m.f.p. is at least the circumference, so disorder is not strong. This necessitates a large interaction strength for EG theory to account for the exponents. If the definition is similar to that of LL theory, i.e. it derives from the electrostatic capacitance of a wire above a ground plane, then the
requirements of being sensitive to the small changes in polymer thickness and the
requirement of strong interaction are conflicting.

Environmental quantum fluctuations (EQF) theory sits well with all the experimental
observations. Offset ohmic characteristics, with a power law at lower voltages,
appearing to originate from the precise geometry of the junction. Reflections in the
MWNT transmission line are generated by the freestanding geometry. The
combination of the impact of these reflections on $Z_{in}(a)$ and the small junction
capacitances means that a significant component of the charge on the junction after a
tunnelling event decays very slowly. Single junction CB is a dynamic effect, slowing
down the tunnelling rate. The slow decay of charge suppresses the tunnelling rate,
appearing as high impedance environment. In this manner, reflections produced by the
freestanding geometry account for the high impedances (exponents) observed. The
small capacitance is the result of line velocity ($\sim 10^5$ ms$^{-1}$), much smaller than the
speed of electromagnetic waves ($\sim 10^8$ ms$^{-1}$).

The original results gained from the non-conventional freestanding set-up have
provided possibly the best demonstration of single junction coulomb blockade theory.
The non-conventional freestanding geometry has, for the first time split the
predictions of a large-N LL and EQF on a quantum transmission line. The power law
in MWNTs appears to have several manifestations, uniting them all in a single
explanation could well be impossible. So while this work may not end the debate on
the origin of the power law in MWNTs it certainly makes a significant contribution.

6.1 Future Work

Having assigned the variability in the experiment’s results to the uncontrolled
thickness of an insulating coating encapsulating the MWNTs, one obvious direction
for future work would be to take control of the insulating layer thickness. This is in
principle quite possible. Park et al (2006) have developed methods for coating
MWNTs with SiO$_2$, where the thickness can be accurately controlled. However,
whilst gaining control of the insulator thickness reduces some of the unknowns, it
introduces others. Measurements of MWNTs with different insulator thickness would
be on different MWNTs (inconsistent $M$) and different probe sizes (inconsistent
$r_{prop}$).
On the theoretical side, the accuracy of the simulations at short wavelengths could be improved to make a more sophisticated, analytical fit to $Z_{de}(\omega)$ worthwhile. Then, employing numerical methods, the IV characteristics could be calculated directly. However, this would require considerable mathematical expertise, and it is likely there would be limited payoff in terms of original research. The calculation could simply confirm the explanation in this thesis. Additionally, if the simulations are made more accurate in their current form (i.e. increasing the transmission line segments from 400 to ~ 40,000), this would be extremely laborious.

While on the subject of further theoretical work, EG theory should be explored. Once again, numerical methods are necessary to obtain a calculated IV. Given the uncertainty surrounding the interaction strength, a top down approach could be taken. Manipulating the parameters (disorder and interaction strength) to produce simulated IV characteristics resembling the measurements, consistency in the parameters with those necessary to reproduce on-substrate exponents could then be the used to evaluate the validity of EG theory.

The role of reflections in the power law phenomenon could be probed further, possibly by creating impedance discontinuities in on-substrate geometries. Discrete and continuous impedance changes could be created with some degree of control. It would also be of interest to apply such an experimental set-up to SWNTs.

The measurements were all conducted before an explanation was shaped, and some were conducted before even the form of the data was identified. The findings in this thesis could well be further strengthened by conducting further measurements.
Bibliography


Avouris, Ph. et al 2006 [presentaion at Nanotube 2006, Nagano Japan].


## Appendix 1: Symbols and Constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>( \eta )</td>
<td>Voltage division factor</td>
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<tr>
<td>( \varrho )</td>
<td>Ratio of free carriers to those trapped</td>
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<td>( \sigma )</td>
<td>Conductivity</td>
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<td>( \langle q^2 \rangle )</td>
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<td>( A )</td>
<td>Part of charge decay function</td>
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<tr>
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<td>Amplitude of slow exponential in charge decay function</td>
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<tr>
<td>$V_{TH}$</td>
<td>Threshold voltage</td>
<td>V</td>
</tr>
<tr>
<td>$x$</td>
<td>Distance</td>
<td>m</td>
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<td>$x_0$</td>
<td>Fitting parameters</td>
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<td>$X_c$</td>
<td>Capacitive reactance</td>
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</tr>
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<td>Line Admittance</td>
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</tr>
<tr>
<td>$Z$</td>
<td>Impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
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<td>-------------</td>
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<td>Impedance of free space ~ 377</td>
<td>Ω</td>
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<td>$Z_{\text{extracted}}$</td>
<td>Impedance extracted from power law exponent</td>
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<td>$Z_{lf}$</td>
<td>Low frequency input impedance</td>
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<td>$Z_{\text{line}}$</td>
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</tr>
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<td>Sub-band separation (energy)</td>
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<tr>
<td>$\Delta I$</td>
<td>Current step or jump in failure of MWNT shells</td>
<td>A</td>
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<tr>
<td>$\Delta k$</td>
<td>Separation of allowed $k$ values</td>
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<tr>
<td>$\Delta Z$</td>
<td>Change in impedance</td>
<td>Ω</td>
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<td>$\Phi$</td>
<td>Barrier height</td>
<td>J</td>
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<td>$\Gamma$</td>
<td>High symmetry point in the Brillouin zone</td>
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<td>$\Gamma$</td>
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</tr>
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<td>Electron reflection co-efficient at the polymer-contact interface</td>
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</tr>
<tr>
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<td>Frequency (phonon)</td>
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<td>$\alpha$</td>
<td>Power law exponent</td>
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<td>Propagation constant</td>
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<td>Symbol</td>
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<td>Delta function, (\delta(0) = \infty, \delta(\neq 0) = 0)</td>
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<td>Permittivity of vacuum or electric constant, 8.854x10(^{-12})</td>
<td>Fm(^{-1})</td>
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<td>Wavelength</td>
<td>m</td>
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<td>Mobility</td>
<td>m(^2)V(^{-1})s(^{-1})</td>
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<td>Contact potential energy</td>
<td>eV or J</td>
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<td>Pi, 3.1416</td>
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<td>Angle between initial state and final state of an electron</td>
<td>°</td>
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<td>Charge density (units given for the 1D case)</td>
<td>Cm(^{-1})</td>
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<td>(\rho_v)</td>
<td>Voltage reflection co-efficient</td>
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<td>(\tau_c)</td>
<td>Average time between collisions</td>
<td>s</td>
</tr>
<tr>
<td>(\tau_d)</td>
<td>Junction discharge time constant</td>
<td>s</td>
</tr>
<tr>
<td>(\tau_{transit})</td>
<td>Tunneling time of electron under barrier</td>
<td>s</td>
</tr>
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<td>(\nu_0)</td>
<td>Non-interacting DOS (units given for 1D)</td>
<td>J(^{-1})m(^{-1})</td>
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<tr>
<td>(\nu(E))</td>
<td>DOS as function of energy (units given for 1D)</td>
<td>J(^{-1})m(^{-1})</td>
</tr>
<tr>
<td>(\omega)</td>
<td>2(\pi)f frequency</td>
<td>s(^{-1})</td>
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</table>
Appendix 2: Line Capacitance

Appendix 2 is a MathCAD document exploring three possible ways to calculate the line capacitance. As it is MathCAD document the equation formatting is slightly different.

Wire Above a Ground Plane

Before considering the situation of the MWNT and the probe, the formula for capacitance is introduced and the circumstance for which it was derived. The capacitance of a wire above a ground plane (Figure A2.1) is given as in (Burke 2002):

\[ C = \frac{2\pi \sigma}{\operatorname{acosh} \left( \frac{2(h + r_{\text{ent}})}{2r_{\text{ent}}} \right)} \]

This is the exact formula, the approximation is given by:

\[ C = \frac{2\pi \sigma}{\ln \left( \frac{h}{2r_{\text{ent}}} \right)} \quad \text{Burke (2002)} \]
\[ C = \frac{2\pi \sigma}{\ln \left( \frac{2h}{2r_{\text{ent}}} \right)} \quad \text{Bockrath (1999)} \]

This can be derived by the \( C = Q / V \) method. Figure A2.1b shows a cross section of Figure 1a with the electric field indicated by the solid lines. Integrating the electric field along the black line in Figure A2.1b, from one of line charges to the ground plane give the potential \( V \), on substitution into \( C = Q / V \) the charge, \( Q \) cancels giving the capacitance.

The key point here is that the formula for the electric field created by a line charge is derived assuming it is infinitely long, i.e. there is no electric field component in parallel to the axis of the line charge.
**Nanotube and Probe**

The aim of this calculation is get the capacitance per length of the MWNT as it glances past the probe. Unless a 3D electrical field simulation is used, it is necessary to simplify the geometry of a nanotube connected to a probe. Fortunately, the geometry of a nanotube connected to a probe lends itself to considerable simplification, as the nanotube is much smaller than the tip. Figure A2.2 shows the situation to which we simplify the MWNT and the probe too. Two intersecting metallic cylinders.

**Figure A2.2: Simplified geometry of a MWNT-probe contact**
This is done to allow us to use the standard formulas for the capacitance of a wire above a ground plane as described above. Explicitly we have made the following simplifications:

**Simplification 1**

**MWNT is perfectly straight.** In reality the MWNT is never perfectly straight, as it is likely that the probe pushes or pulls the MWNT perpendicular to the focal plane in the SEM. However MWNTs are very rigid (Hertel et al 1998) and bends, with radius on the scale of the probe radius are not generally possible, so it is quite reasonable to assume that the MWNT is straight on the scale of 1 µm or so.

**Simplification 2**

**The MWNT and the probe axis are perpendicular.** Given that we have defined the probe diameter as the overlap distance, between the MWNT and probe this assumption seems perfectly reasonable.

**Simplification 3**

**The wire above a ground plane is applicable.** This simplification is reasonable where the MWNT and the probe are closest provided that the minimum separation, \( t_{\text{poly}} \) is much less than the probe diameter, \( t_{\text{poly}} \ll r_{\text{probe}} \). This inequality is well satisfied in our situation as typical probe radius is 200 nm and the polymer thickness in the range of 0 to 30 nm. However further away from point of minimum separation, the field will have significant a component parallel to axis if the MWNT. This is discussed later.

**Simplification 4**

**The probe is modelled as a cylinder rather than a cone.** This is shown in cross-section in Figure A2.3, the 'realistic' situation depicted in (a) and the simplification in (b). This is a reasonable simplification given that the probes come to a point very slowly relative to width of the MWNT, and unless the cone was extraordinary steep the extra contribution to the capacitance on the right would be cancelled by the reduced contribution on the left.


Figure A2.3: Cross-section along probe axis (i.e. normal to tube axis)

**Calculation of $h$, Distance Above Ground Plane**

The height above the ground plane and therefore the capacitance can be defined in several ways, $h_1$ to $h_3$ as shown in Figure A2.4. We define the $x$ axis to be the MWNT axis and $x$ to be zero where the MWNT and the probe are closest. And then calculate $h(x)$

![Diagram of cross-section along probe axis](image)

**Figure A2.4: Different definitions of $h$**

Define some typical values;

$ r_{probe} = 300 \times 10^{-9} $ Probes Radius
Paul Smith

Appendix 2: Line Capacitance

\[ t_{\text{poly}} = 10^{-9} \quad \text{Polymer thickness or minimum probe-MWNT separation} \]

\[ r_{\text{cnt}} = 7 \times 10^{-9} \quad \text{MWNT radius} \]

First Method, \( h_1 \)

Possibly the most obvious definition is the vertical distance between point \( x \) on the MWNT and the probe surface. A little trigonometry is used to define an intermediate function \( y(x,r_{\text{tip}}) \). However as \( x \) approaches the probe radius simplification 4 is compromised, and the capacitance cannot be defined for \( x > r_{\text{probe}} \).

\[ y(x,r_{\text{probe}}) = r_{\text{probe}} - r_{\text{probe}} \cos \left( \sin \left( \frac{x}{r_{\text{probe}}} \right) \right) \]

\[ h_1(x) = t_{\text{poly}} + r_{\text{cnt}} + y(x,r_{\text{probe}}) \]

Second Method, \( h_2 \)

This is defined as the shortest distance between \( x \) and the probe which is defined approximately using Pythagoras rule. This definition has the advantage of giving values for \( x > r_{\text{probe}} \).

\[ h_2(x) = r_{\text{cnt}} + \sqrt{\left( t_{\text{poly}} + r_{\text{probe}} \right)^2 + x^2} \quad \text{Error negligible} \]

Third Method, \( h_3 \)

The formula shown at the start is for the capacitance between the ground plane and the wire it can also be considered as the self-capacitance of the wire. Further to this if no ground plane is present, the length of the wire can be substituted into \( h \), giving the self capacitance of a truly freestanding wire this is how \( h_3 \) is defined.

Results

Define constant

\[ \varepsilon_0 = 8.854 \times 10^{-12} \, \text{F m}^{-1} \text{ Electric Constant} \]
Redefine Capacitance, now that other capacitance have been defined

\[ C_{\text{es}, l}(h) := \frac{2 \pi \varepsilon}{\cosh \left( \frac{2 h}{2 r_{\text{nt}}} \right)} \]

Define x range

Figure A2.5: h vs. x, distance along the MWNT. h₁ (solid red), h₂ (dotted blue) and h₃ (dashed green).
Figure A2.6: Line capacitance vs. distance along the MWNT. $h_1$ (solid red), $h_2$ (dotted blue) and $h_3$ (dashed green).

**Conclusions**

It does not seem reasonable to use $h_3$, the freestanding wire for $x \sim 0$ as the similarity to a wire above a ground plane is good, however $h_1$, is clearly a poor approximation for $x \sim r_{\text{probe}}$, and this leaves $h_2$ as the best choice, replicating $h_1$ and $h_3$ where they are most valid.
Appendix 3: Polymer Breakdown

Introduction

The widespread use of polymers as electrical insulation makes their electrical breakdown of obvious industrial importance; however this has not translated into a satisfactory understanding of breakdown phenomena in polymers. Electrical breakdown appears to be dependant on many factors, and the complete life history of a sample is not least amongst them. For these reasons we will restrict ourselves to answering a specific question:

Could the conduction mechanism in the polymer be responsible for the IV characteristics i.e. the power law and offset ohmic behaviour?

It is of course, impossible to prove a negative answer to this question, so the best that can be done is to investigate and exclude the possible/probable conduction mechanisms. Whether these mechanisms constitute ‘breakdown’ is perhaps a matter of perspective, as is the whole notion of breakdown when considering polystyrene thickness of a few 10’s of nm at most. If we are defining breakdown as some rapid increase in current, the consequences of which are catastrophic and irreversible for the material, none of the conduction mechanisms below are a breakdown of the material, actually breakdown of the material may occur before some of these mechanisms would be expected to dominate conduction.

Before considering specific mechanisms some background is in order, with a quote from Dissado and Fothergill (1992), a source for much of the material in this section. “Energy band theory was originally developed to explain electron energies in crystalline materials, and subsequently used extensively in semiconductor theory and has evolved, but not entirely satisfactorily, to encompass semi-crystalline and amorphous materials.”. One of the most important modifications to energy band theory for materials like insulating polymers is the introduction of localised states.

Figure A3.1 is a typical example of the band diagram found in introductory textbooks, but with the addition of localised trap states, shown as open squares at an energy level $E_t$. The conduction and valance bands are delocalised, with the size of the band gap ($E_g = E_c - E_v$), determining whether this material would be considered a semiconductor.
or insulator. The positions of the band edges and traps states (if present), relative to Fermi level, $E_F$ will determine the ohmic conductivity.

![Energy band diagram and density of states](image)

**Figure A3.1:** Energy band diagram and density of states for a crystalline insulator or semiconductor with localised states below the conduction band level shown as open squares.

The band structure model in Figure A3.1 is not generally a realistic model for insulating polymers, it is perhaps more appropriate for a crystalline insulator with a particular impurity of defect which will produce trap sites at the same energy. Figure A3.2 is a much more suitable model for an insulating polymer, once again the trap sites shown by open squares, delocalised bands are absent, however the concentration of localised states in close proximity to each other is analogous to the delocalised conduction and valance bands in Figure A3.1. Although it is possible to calculate the band structure for a single isolated polymer molecule this is not generally found to be representative, in the random arrangement of the bulk material, where the polymer chains are distorted. While there is a state that can be delocalised on a single molecule, in general they do not delocalise between molecules. The result is that there can be almost as many trap states as there are atoms.
Figure A3.2: A schematic diagram showing localised states in a non-crystalline material (indicated by squares) as a function of electron energy together with the density of states $n(E)$ and the mobility $\mu(E)$. The overlap of squares represents where carriers can easily move between states. Reproduced from Figure 2.6, p39 of Dissado and Fothergill (1992).

How the electronic structure of insulating polymers can be modelled has been introduced by Figure A3.1 and Figure A3.2, but before the specifics of any conduction mechanism are discussed we need to return the focus back to purpose of this section.

The number and quality of the fits to the data presented in chapter 4 very strongly suggests that a power law and offset ohmic is the correct way to interpret the data, so the question is could these characteristics be interpreted as another conduction mechanism? Just as power law dependencies are best observed on a log $J$ vs. log $V$ plot and offset ohmic on linear–linear scales, many of conduction mechanisms that follow are best observed on their own specific plot, with quantities and scales chosen to produce straight lines. In several cases, it is appropriate show the power law and offset ohmic characteristics on these specific plots; this will be done employing the fits shown Figure 4.15. Although the power law is only followed for a couple of orders of magnitude before it crosses over to the offset ohmic in this case. Many samples fit a power law over a wider range so additionally the full extent of the power law fit displayed (as in Figure 4.15) and can be considered when assessing whether
these data fits follow a straight line on the plots specific to a particular conduction mechanism. The classification and structure of the conduction mechanisms presented below is the same as that in Dissado and Fothergill (1992).

**Low Field Conduction Mechanisms**

**Ohmic - Trap Free**

This is normal ohmic conduction within a delocalised band, e.g. Figure A3.1 with no traps, \( I \propto V \):

\[
J = n \cdot e \cdot \mu \cdot E
\]  

(88)

Where, \( e \) is charge on an electron and \( E \) the electric field. The conductivity, \( \sigma = n e \mu \) determined by the carrier concentration, \( n \) and the mobility, \( \mu \). The carrier concentration in turn is determined by the density of states, \( n(E) \) and the Fermi-Dirac distribution, (probability of finding an electron at energy, \( \Delta E \) away from the Fermi level, \( E_F \) at a temperature \( T \)). The mobility is defined by some average drift velocity \( v_{\text{drift}} \), which is dependant on electric field \( E \):

\[
\mu = \frac{v_{\text{drift}}}{E} = \frac{e \tau_c E}{m^* E}
\]  

(89)

Where the average time between collisions is \( \tau_c \) and the effective mass is \( m^* \). A typical mobility for an insulating polymer is \( 10^{-15} - 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \), which is very low, this because the delocalised band model is not appropriate. Figure A3.2 is more realistic representation of the electronic states in an insulating polymer, it shows there are very few neighbouring states near the centre of the gap (where the Fermi level is likely to reside) and this makes it difficult for charge to move from one localised state to another, if the Fermi level were closer to the energy levels where localised states are clustered, the delocalised band model may make a better approximation. However since the Fermi level is near the centre of the gap, it is difficult for carriers to move from one localised state to another, effectively \( v_{\text{drift}} \) is very low and therefore so is the mobility, \( \mu' = E_F \) when the conduction is modelled this way.

True ohmic conduction is unlikely in polymers even if \( I \propto V \), as the temperature dependences typically found for insulating polymers are not in agreement with the...
ohmic energy band conduction model. In terms of our results ohmic conduction is only able to explain the first part of the power law behaviour, i.e. when \( I \propto V^4 \).

**Ohmic – With Trap Limited Mobility**

This is derived based on Figure A3.1 with the traps included, the result is still ohmic conductivity, i.e. equation (88), but it is multiplied by a factor, \( \theta \), which can be very small \( (10^{-10} - 10^{-6}) \). \( \theta \) is ratio of carriers in the conduction band to those in the traps:

\[
\theta = \frac{n_c}{n_t}
\]

(90)

Where \( n_c \) is carrier concentration in the delocalised conduction band and \( n_t \) is carrier concentration in the localised trap states. Because the free carrier concentration has dropped, i.e. electrons spend most of their time in the traps, not as free carriers. It is actually a trap limited carrier concentration rather than trap limited mobility.

**Ionic Conduction**

An ionic current is formed by ions percolating through the polymer and giving up their charge to an electrode, this process could indeed contribute to the current, but it can easily be ruled from producing a significant contribution in our case. Although ions can carry charge of several multiplies of \( e \), the supply of ions is always finite (unless the MWNT is or tungsten probe is supplying ions). Estimating the volume of polystyrene to be a 30nm cube (which is 27000 nm\(^3\)) the number of atoms in this volume can be calculated \( (\sim 10^6 \text{, with the density of polystyrene 1050 kgm}^{-3}) \). This will give an absolute limit to the number of ions. The charge transported in half an \( IV \) measurement is \( \sim 10^{14}xe \), so with around \( 10^6 \) atoms there is simply not enough ions for an ionic current to be responsible for the \( IV \) characteristic, even if our assumption of the volume material is several orders of magnitude wrong.

**Charge Injection from Electrodes**

In some circumstances it is not the conduction in the polymer bulk which controls the conductance but the charge injection into the bulk. There are two mechanisms in Dissado and Fothergill (1992); Schottky emission and Fowler Nordheim emission sometimes referred to as field emission. Both of these are derived in Dissado and Fothergill (1992) with none of complications found in real electrode-insulator
interfaces, the following sub-sections summarise the mechanisms as they presented in Dissado and Fothergill (1992).

**Schottky Emission**

At the interface between a metal electrode and insulator is a barrier which the electrons in the metal must surmount for conduction to proceed. The barrier height is determined by the difference in work function of the metal ($E_{\text{vac}} - E_F$) and the electron affinity of the insulator ($E_{\text{vac}} - E_C$). The shape is influenced by the mismatch of the $E_{\text{vac}}$ for the metal and the insulator. The Schottky effect is an image charge effect which changes the shape of barrier and can actually lower its height as can be seen in Figure A3.3.

![Image of Schottky Emission](image)

**Figure A3.3:** Barrier lowering from Schottky effect. The figure is a modified version of that appearing in Sze (1981). Without accounting for the Schottky image charge effect and the electric field (dashed lines) the energy barrier would follow the energy-distance axis, the resultant barrier after the superposition of these effects is shown by the solid line, the barrier height has been reduced by $e\Delta \Phi$. 

- 209 -
The probability an electron has enough energy to surmount the barrier is always finite, but much enhanced by a lower barrier height. The current density predicted from Schottky emission is given by:

\[ J = \frac{4 \cdot \pi \cdot e \cdot m \cdot k_B^2 \cdot (1 - \Gamma_c) \cdot T^2}{h^3} \cdot \exp \left( \frac{-e \cdot \Phi}{k_B \cdot T} \right) \cdot \exp \left( \frac{e}{2 \cdot k_B \cdot T} \cdot \left( \frac{eE}{\pi \cdot \varepsilon_0 \cdot \varepsilon_r} \right)^{1/2} \right) \] (91)

Where \( \Gamma_c \) is the reflection co-efficient for electrons at the polymer contact interface.

To look for Schottky emission the measurement a plot of \( \ln(J/T^2) \) vs. \( E^{1/2} \) is constructed. This should yield a straight line whose gradient and intercept can be identified from equation (91) re-arranged:

\[ \ln(J/T^2) = \ln \left( \frac{4 \cdot \pi \cdot e \cdot m \cdot k_B^2 \cdot (1 - \Gamma_c)}{h^3} \right) + \frac{e \cdot \Phi}{k_B \cdot T} + \frac{e}{2 \cdot k_B \cdot T} \cdot \left( \frac{e}{\pi \cdot \varepsilon_0 \cdot \varepsilon_r} \right)^{1/2} \cdot E^{1/2} \] (92)

Figure A3.4 shows the power law and offset ohmic fits on Schottky plot axis, neither produces a straight line, Schottky injection into the polymer cannot therefore explain any aspect of the IV characteristic.

Figure A3.4: Power Law (solid red) and offset ohmic (dashed blue) with Schottky plot axis.
**Fowler-Nordheim Emission**

Fowler-Nordheim injection or field emission is also based on Figure A3.3, with the application of electric fields the barrier width at $E_F$ becomes finite and with large enough fields, so thin, that there is a significant probability that an electron can tunnel through it. Field emission is an electron tunnelling through this barrier rather than gaining enough energy to go over it as in Schottky emission. The Fowler-Nordheim equation is reproduced as in Dissado and Fothergill (1992): -

$$ J = \frac{e^3 \cdot E^2}{8 \cdot \pi \cdot h \cdot \phi} \cdot \exp \left( -\frac{4}{3} \cdot \left( \frac{2 \cdot m}{\hbar^2} \right)^{\frac{1}{2}} \cdot \frac{\phi^{\frac{3}{2}}}{e \cdot E} \right) $$

(93)

Re-arranged to give straight line with a negative gradient by plotting $\ln(I/V^2)$ vs $1/V$.

$$ \ln \left( \frac{J}{E^2} \right) = \ln \left( \frac{e^3}{8 \cdot \pi \cdot h \cdot \phi} \right) - \frac{4}{3} \cdot \left( \frac{2 \cdot m}{\hbar^2} \right)^{\frac{1}{2}} \cdot \frac{\phi^{\frac{3}{2}}}{e} \cdot \frac{1}{E} $$

(94)

As Figure A3.5 clearly shows when the power law and offset ohmic fits are plotted on Fowler-Nordheim axis nothing close to a straight line is produced.

![Figure A3.5: Fowler-Nordheim plots with Power Law (solid red) and offset ohmic (dashed blue). Both panels show the same data fits, just different horizontal axis ranges.](image)

**High Field Conduction Mechanisms**

**Space Charge Limited current**

Space charge limited is not a conduction mechanism in the sense that those discussed previously are, it arises from an upper limit on the charge that can be injected into
insulator, and this limit on charge dictates the shape of the IV. Considering only the charge injection mechanism in isolation (e.g. field emission) can lead to a prediction of so much charge entering the insulator that the electric field at the injecting electrode is reduced or even neutralised. Figure A3.6 illustrates a uniformly distributed (single carrier) space charge which reduces the field at the injecting electrode to zero.

Figure A3.6: a) Accumulation of charge on each side of insulator (\( \rho \) is charge density) producing a uniform electric field, \( E \) in the insulator. b) Space charge that is uniformly distributed throughout the insulator such that there is no electric field at the injecting electrode interface.
Summarising the derivation for space charge limited conduction from Rose (1955):
Consider the insulator sandwiched between the electrodes, a simple parallel plate capacitor is formed, which will hold a charge, \( Q \):

\[
Q = V \cdot C
\]  

(95)

This sets the limit for charge in the insulator, an amount of charge greater than \( Q \) would not enter the insulator, there would be no field and hence no accumulation at the charge injecting electrode. The maximum current that traverse the insulator is then set by:

\[
I = \frac{Q}{T_{\text{transit}}}
\]  

(96)

Where \( T_{\text{transit}} \) is the time for charge \( Q \) to traverse the insulator:

\[
T_{\text{transit}} = \frac{t_{\text{poly}}}{v_{\text{drift}}} = \frac{t_{\text{poly}}}{\mu \cdot E} = \frac{t_{\text{poly}}^2}{V \cdot \mu}
\]  

(97)

Where of thickness, \( t_{\text{poly}} \) is the insulator thickness. Substituting in the formula for a parallel plate capacitor, equations (95), (96) and (97) lead to a current dependant on the square of voltage:

\[
J = \frac{9 \cdot E_0 \cdot \varepsilon_r \cdot \mu \cdot V^2}{8 \cdot t_{\text{poly}}^3}
\]  

(98)

In this simplified derivation, much has been neglected. Equation (98) is for trap free dielectrics, with the space charge evenly distributed throughout the insulator and the contacts are ohmic. Ohmic, in this case means that charge can easily be injected into the insulator. In practice “whether space charge limited current becomes the ‘rate determining step’ controlling current between the electrodes will depend on the charge concentration, the type of charge, its mobility, how good the electrodes are at injecting charge, and the trapping characteristics.” – Dissado and Fothergill (1992).

If the current is considered to have two components, an ohmic and a space charge limited, then the transition from an ohmic current to space charge is occurs at a voltage \( V'_n \):

\[
V'_n = \frac{8 \cdot e \cdot n_0 \cdot t_{\text{poly}}^2}{9 \cdot E_0 \cdot \varepsilon_r}
\]  

(99)
Where \( n_0 \) is the intrinsic carrier concentration, i.e. carrier concentration in the conduction band when \( V \to 0 \). The transition occurs when the carrier concentration due to injection from the electrode, \( n_1 \) is greater than \( n_0 \), \( n_1 > n_0 \). This means that space charge controls the field distribution within the insulator.

Space charge limited conduction in the case of a dielectric with traps (at a single level below the conduction band) is modified in much the same way that ohmic conduction was. The difference is the factor \( \theta \), defined previously in equation (90), it is the ratio of carriers in the conduction band to those in traps.

\[
J = \theta \cdot \frac{9 \cdot e_0 \cdot \varepsilon_r \cdot \mu \cdot V^2}{8 \cdot t_{poly}^3}
\]  

(100)

Correspondingly equation (99) is multiplied by the factor \( \theta^4 \) for an insulator with traps. The other modification to the \( IV \) characteristic resulting from the inclusion of traps is that when the carrier injection becomes large enough the traps can become completely filled, resulting in a very rapid increase in current (\( dI/dV \to \infty \) when all traps at a single level), once the traps have been filled the current goes as \( J \propto V^2 \) once more, following equation (98). This is all shown in Figure A3.7, which shows the how different the \( IV \) characteristic is with the addition of traps, lower current, higher transition voltage between ohmic and space-charge-limited and the trap filled discontinuity.
Figure A3.7: The dashed lines create a triangle in which the IV characteristic must lie, the minimum current is given by ohmic conduction $I \propto V^1$ and the maximum by child's law for solids, (equation (98)) $I \propto V^2$. The right hand border is set by the trap filled limit. The two IV curves shown in solid black are theoretical results for a CdS crystal, an insulator with traps at a single level, the curves correspond to traps at 0.5 and 0.6eV below the conduction band. These results follow equation (100), current is still proportional to voltage squared by the actual current is lower by the factor $\theta$. The higher crossover voltage from ohmic to space charge limited should also be noted. This figure is a modified version of figure 5 in Lampert, (1956).

The rapid increase in current at the trap filled limit can be though of as $\theta$, rapidly changing from its typically very small value ($10^{-10}$-$10^{-6}$), to unity. It is completely unrealistic that all the traps are at a single level in an amorphous polymer such as polystyrene. What this means is that for more realistic cases where traps are distributed across a range of energies the traps filled limit is reached gradually, making $\theta$, a function of voltage. If the density of traps reduces form the conduction band edge a power law should be observed in the triangle of Figure A3.7, (Rose 1955), rather than the normal square law.
\[ I \propto V^{T/T_c} \]  \hspace{1cm} (101)

\[ T_c \geq T \]

Where \( T \) is the measurement temperature and \( T_c \) is a characteristic temperature greater than the measurement temperature. The value of \( T_c \) reflects the distribution of traps below the conduction band edge. A small \( T_c \) is rapidly varying trap distribution while a high \( T_c \) is for slowly varying trap distribution. The result is current proportional to a high power of voltage, i.e. greater than two.

Of all the mechanisms discussed here space-charge-limited conduction compares best to the characteristics of polystyrene films as measured by Burnmester and Caldecourt (1968). Directly measuring the \( IV \) characteristic as we have done was not possible in the study by Burnmester and Caldecourt (1968), large time-dependent polarization currents make measurements of the steady state current in this way impossible. Measurements were made on samples of various thickness, (minimum 100nm) prepared by a two different methods and measured in three different configurations, they were all well fitted by a power law, equation (102), with an exponent of 3.5 or 2.5 if it defined as \( I \propto V^{3.5} \).

\[ J = 1.5 \times 10^{-33} \cdot E^{3.5} \]  \hspace{1cm} (102)

The power law was followed between fields of 8 – 200 V\( \mu \)m\(^{-1}\). Breakdown occurred beyond 200 V\( \mu \)m\(^{-1}\) even in the thinner films that can withstand higher fields (references within Burnmester and Caldecourt 1968). No sign of the trap filled discontinuity was observed. Below fields of 8 V\( \mu \)m\(^{-1}\) the current decreased faster than the power law, indicating no measurable intrinsic ohmic-like conductivity.

Apart from the power law suggested by Rose (1955), Burnmester and Caldecourt, (1968) also suggested a cubic relation, \( I \propto V^3 \) found by Lindmayer and Slobodskoy (1963) could also offer an explanation for the power law. This cubic relation for space-charge-limited conduction was derived including both carrier species and diffusion, these are complications that have not been included in the previous space-charge derivations, however the simplification of a trap free insulator was made.

The specific form of space-charge-limited conduction proposed by Rose (1955) for a crystalline insulator with a distribution of traps below the conduction band could provide an explanation for the power law found in our results, the typically high
exponents and with the exponent being dependant on the distribution of trap sites, there is a possible explanation for the variety of exponents too. Whether this variety is physically reasonable is another question? With the re-arrangement of the polymer, a re-arrangement of traps is intuitively expected, as discussed within section 5.1 structural changes in the polymer are reasonable. However more than a re-arrangement of traps sites is needed, a re-distribution is required for the exponent to significantly change. Whether a re-distribution if trap sites is physically possible or likely is much harder question to answer, and out of scope of this work.

Ohmic conduction, or more generally a mechanism which gives $I \propto V$, that relies on the intrinsic carrier concentration could be possible at low fields, although no such mechanism appeared to be at work in the experiments of Burmester and Caldecourt (1968). So qualitatively there may be an explanation for the ohmic ($I \propto V^1$) and the power law regions ($I \propto V^{\alpha+1}$), however there appears no explanation for offset ohmic portion of our results. The only mechanism which could reign in the current predicted by the power law, is the trap filled limit, although the current may increase rapidly here, Child's law for solids will limit the current to square law. If we ignore for the moment the results where an offset ohmic characteristic is seen for many times $E_C$ and look at the measurements where only the beginnings of a deviation from the power law is visible one could make an argument that this should be interpreted as a transition to Childs law.

This transition to Child’s law should occur at a voltage $V_{TFL}$ Lampert (1956):

$$V_{TFL} = \frac{e \cdot t \cdot \tau_{poly}^2 \cdot N_t}{2 \cdot \varepsilon} \quad (103)$$

Where $N_t$ is total trap density. Setting $V_{TFL}$ to 1V, which is of the order of the charging energies, $E_C$ found in our results, the polymer thickness was set to 10nm, $N_t$ would have be, $2 \times 10^{24}$ m$^{-3}$. That corresponds to 2 traps in a 10nm cube, even if a larger volume of polystyrene is considered we are still left with very few traps, with which to produce a trap distribution that could in turn give rise to the power law at lower voltages, rather than a step like function.

Having tried, to move the vertical side of IV triangle in Figure A3.7 into the same quantitative region as our results the same can be done for the upper boundary, Child’s law. Equation (98) is slightly modified, instead of combining equations (95),
(96) and (97) with the parallel plate capacitor it is combined with the wire above a ground plane capacitance, equation (76). To obtain the current we also need to assume a mobility, $\mu$, in addition to the geometry. First we will assume a geometry, a 7nm radius tube, 10nm polymer thickness and a 10nm length of carbon nanotube, in order to gain quantitatively similar results we need a mobility of around $10^{-5}$ m$^2$V$^{-1}$s$^{-1}$. Alternatively we can assume a mobility at the upper end of those reported for insulating polymers, $10^{-8}$ m$^2$V$^{-1}$s$^{-1}$ (Dissado and Fothergill 1992) although mobilities above $10^{-10}$ m$^2$V$^{-1}$s$^{-1}$ even at high fields are rare. With the mobility set at $10^{-8}$ m$^2$V$^{-1}$s$^{-1}$, a contact 200 nm long and a polymer thickness of just 3 nm is necessary. In the later case the contact geometry is not too realistic, and Child’s law applies when traps are not effective, the reported mobilities or insulting polymers are artificially low due to the presences traps reducing the free carrier concentration, so whether such low mobility should be used may be questionable. When assuming a reasonable geometry, the mobility has to be around $10^{-3}$ m$^2$V$^{-1}$s$^{-1}$, (which very low compared to electrons in Silicon, 0.15 m$^2$V$^{-1}$s$^{-1}$), this mobility is an order of magnitude smaller than the minimum mobility derived in Dissado and Fothergill (1992), assuming the mean free path should be at least 0.2nm, the minimum mobility follows and should be $10^{-3}$-10$^{-4}$ m$^2$V$^{-1}$s$^{-1}$. In trying to set Child’s law to predict similar currents to the offset ohmic ones seen in our results we end up with unrealistic contact geometries even at the highest reported mobility for insulating polymers, or an unrealistic mobility for a plausible contact geometry.

Using equation (102) it is possible to make a quantitative comparison between our results and those of Burnmester and Caldecourt, (1968), for the power laws to occur at similar voltages and currents, would require a film of polystyrene approximately 1cm$^2$ and 1nm thick. However the thickness and area are traded off this is many orders of magnitude off any plausible size for the barrier between the MWNT and probe. From this alone we can conclude the conduction mechanisms at work in the polystyrene films measured by Burnmester and Caldecourt, (1968) and our own results are not the same.

**Hopping conduction**

Variable range hopping can occur between localised states, close to the Fermi level, in a wide band or mobility gap material such as that in Figure A3.2. It can also occur in
smaller band gap materials, but when the Fermi level is closer to tails of states at the mobility edge other process are likely to dominate the conduction. With the localised states near the Fermi level, and many $k_B T$ below the band or mobility edge the barrier from one state to another is too high to be surmounted by energy gained form lattice vibration. Conduction therefore takes place between these localised states near the Fermi level by thermally assisted tunnelling, tunnelling alone is not a significant process above $T = 0 \, K$ as the energy levels of the states are unlikely to be same. If the energy levels are within $k_B T$ or so, it's probable that a carrier may be at the right energy to tunnel between the localised states. The conductivity is therefore dictated by two probabilities, the tunnelling probability, exponentially decreasing with distance, $R_{\text{trap}}$ from the localised state, and the second probability of encountering another state within a distance $R_{\text{trap}}$ which has a similar energy level, this naturally increases with $R_{\text{trap}}$. Temperature obviously plays an important role, smearing the energy levels of the states, lower temperatures necessitating a pair of states have more closely matched energy levels for a tunnelling event to be probable. So conductivity is function of temperature but not of voltage. Therefore variable range hopping could only explain ohmic behaviour, i.e. the $I \propto V$ region.

Poole Frenkle Conduction

This is the bulk analogue of the Schottky effect. Potential wells created by the trap sites are shaped by image charge, Figure A3.8. Trap levels may be many $k_B T$ below $E_c$. The barrier height, $\Phi$ is lowered by the electric field as in Schottky effect. Once again plotting $\ln I$ vs. $V^{1/2}$ should give a straight line. The conclusions are the same as section before, power law and offset ohmic do not produce a straight line on this axis, so Poole-Frenkle conduction is unlikely to be responsible for the $IV$ characteristic.
Appendix 3: Polymer Breakdown

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Figure A3.8: Poole-Frenkle conduction. Solid black lines show the potential well with no electric field, the height of the barrier for the electron is $\Phi$. When the potential well is superimposed with the potential due to the electric field (dash-dot line) the resulting potential (dashed line) shows the barrier to be reduced by $\Delta \Phi$ in the direction of the electric field.

Conclusions

In seeking an alternative explanation for the IV characteristics in conduction mechanisms of insulators, we have found only one mechanism, a specific form of space-charge-limited conduction which warranted deeper investigation and some debate.

Qualitatively, there are conduction mechanisms such as ohmic or variable range hopping which could explain the first part of the IV measurement, ($I \propto V^1$), space charge limited conduction with a distribution of traps within the band gap could also explain the second part of the IV measurement ($I \propto V^{2+}$). The third part of the IV measurement, the offset ohmic bit needs to be regarded as a misinterpretation of the data in order for this part of the IV measurement to be explained within the space charge limited conduction picture. However as can be seen from Figure 4.17 through to Figure 4.19, offset ohmic is the correct interpretation.

An accurate quantitative analysis can easily be frustrated by uncertainties over the mobility values, the number and location of traps sites, etc. The limited quantitative analysis that was done, trying to move the IV triangle in Figure A3.7 into the same
region as our results required unreasonable values for mobility, contact size and trap density. Despite all these parameters having wide range of plausible values. Given the variety seen in our results which to some degree is expected given the experiment, any explanation needs to use realistic values, which have room to change, the polystyrene thickness, \( t_{\text{poly}} \) being a prime example, finding an explanation that works with parameters at or beyond their plausible extremes is no good. Finally, the comparison with the measurements of polystyrene films, where the same conduction mechanisms discussed here could be operating revealed a massive difference. Despite the promise of a power law with a large and variable exponent, it does not appear that a conduction mechanism associated with the polystyrene can explain our results.