Mechanical behaviour of carbon nanostructures

Henrik Jackman
Mechanical behaviour of carbon nanostructures

Henrik Jackman
Mechanical behaviour of carbon nanostructures

Henrik Jackman

DISSERTATION

urn:nbn:se:kau:diva-32041

Karlstad University Studies | 2014:33

ISSN 1403-8099


© The author

Distribution:
Karlstad University
Faculty of Health, Science and Technology
Department of Engineering and Chemical Sciences
SE-651 88 Karlstad, Sweden
+46 54 700 10 00

Print: Universitetstryckeriet, Karlstad 2014

WWW.KAU.SE
Abstract

Carbon nanotubes (CNTs) have extraordinary mechanical and electrical properties. Together with their small dimensions and low density, they are attractive candidates for building blocks in future nanoelectromechanical systems and for many other applications. The extraordinary properties are however only attained by perfectly crystalline CNTs and quickly deteriorate when defects are introduced to the structure. The growth technique affects the crystallinity where in general CNTs grown by arc-discharge are close to perfectly crystalline, while CVD-grown CNTs have large defect densities. Mechanical deformation also affects these properties, even without introducing defects. When CNTs are bent they behave similarly to drinking straws, i.e. they buckle or ripple and their bending stiffness drops abruptly.

In this thesis, the mechanical behaviour of individual CNTs and vertically aligned carbon nanofibers (VACNFs) has been studied by performing force measurements inside electron microscopes. Cantilevered CNTs, and VACNFs, were bent using a force sensor, yielding force-deflection curves while their structure was imaged simultaneously.

We have found that CNTs grown by arc-discharge have a high enough crystallinity to possess a Youngs modulus close to the ideal value of 1 TPa. CVD-grown CNTs possess a Youngs modulus that is about one order of magnitude smaller, due to their large defect density. The VACNFs are yet another order of magnitude softer as a result of their cup-stacked internal structure. We also found that a high defect density will increase the critical strain for the rippling onset and the relative post-rippling stiffness. For highly crystalline CNTs, we found unexpectedly large variations in the onset of rippling, where multi-walled CNTs with a small inner diameter are less prone to ripple. In the rippled phase the relative bending stiffness is mainly dependent on the deformation mechanism, i.e. rippling or buckling.
Acknowledgements

First I would like to thank my supervisor Krister Svensson for giving me the opportunity to pursue my career as a PhD student. You have always found the time to help me when I had questions and your passion for physics has been inspiring. I am also grateful to my second supervisor Pavel Krakhamalev for having the patience to read through and comment on, what has sometimes felt like, endless versions of our manuscripts.

I also would like to thank Farzan Ghavanini and Peter Enoksson at the Chalmers University of Technology for the synthesis of the VACNF samples, without your contribution there would obviously not have been a project.

I am also thankful to all the present and former staff at the Department of Engineering and Physics for making every day at work enjoyable.

Thanks also to my family and friends for helping me relax from my studies and keep contact with the world outside the microscopy room.

Finally I would like to thank Victoria for putting up with me during the time I wrote this thesis.
List of publications

This thesis is based on the work done in the following appended publications:


The author of this thesis was responsible for most of the writing and carried out all of the experimental work and analysis in publications I, II, IV and V.

In publication III, the contribution from the author was performing the mechanical measurements and doing some of the analysis and writing some parts of the paper.
Contents

Acronyms vii

1 Introduction 1

2 Background 5
  2.1 History 5
  2.2 Carbon structures 6
  2.3 Structure of CNTs 7
  2.4 Properties 9
    2.4.1 Electronic properties 9
    2.4.2 Mechanical properties 9
      2.4.2.1 Experimental 11
      2.4.2.2 Theoretical 16
  2.5 Applications 19
    2.5.1 Electrical 19
    2.5.2 Mechanical 19
    2.5.3 Nanoelectromechanical systems 20

3 Experimental 23
  3.1 Electron microscopy 23
    3.1.1 Electron gun 24
    3.1.2 Electromagnetic lenses 25
  3.2 Scanning electron microscopy 28
    3.2.1 Beam-specimen interaction 29
    3.2.2 Beam interaction with carbon nanotubes 30
      3.2.2.1 Simulation 32
**Acronyms**

\[\begin{array}{ll}
\alpha & \text{Taperedness factor} \\
\delta & \text{Displacement} \\
\Gamma & \text{Full width at half maximum} \\
\varepsilon_{cr} & \text{Critical strain} \\
d & \text{Diameter} \\
E & \text{Young’s modulus} \\
F & \text{Force} \\
l & \text{Intensity} \\
k & \text{Spring constant} \\
l_{cr} & \text{Critical length} \\
r & \text{Radius} \\
t_N & \text{Normalized thickness} \\
AFM & \text{Atomic force microscopy / microscope} \\
\end{array}\]

- **BSE**: Backscattered electrons
- **CCVD**: Catalytic chemical vapor deposition
- **CNF**: Carbon nanofiber
- **CNT**: Carbon nanotube
- **CVD**: Chemical vapor deposition
- **EBID**: Electron beam-induced deposition
- **f-CNT**: Functionalized carbon nanotube
- **FEG**: Field emission gun
- **FEM**: Finite element method
- **FFT**: Fast Fourier transform
- **MD**: Molecular dynamics
- **MWCNT**: Multi-walled carbon nanotube
- **NEMS**: Nanoelectromechanical systems
- **SE**: Secondary electron
- **SEM**: Scanning electron microscopy / microscope
- **SWCNT**: Single-walled carbon nanotube
- **TEM**: Transmission electron microscopy / microscope
- **VACNF**: Vertically aligned carbon nanofiber
- **VLS**: Vapor-liquid-solid
Chapter 1

Introduction

If not familiar to carbon nanotubes (CNTs) one could, given the name, guess that it is a small tube (nano means a billionth) made up of carbon, and that is just what it is. A single walled carbon nanotube (SWCNT) can be seen as one atomic layer of carbon (graphene) in the shape of a tube. A CNT can also consist of several concentric tubes and is then referred to as a multi-walled carbon nanotube (MWCNT). The diameter of CNTs ranges from about 1 nm to 100 nm, and their lengths can be up to a couple of centimetres. Their typical length is however a few micrometers.

The large scientific community was introduced to carbon nanotubes in 1991 [1] and since then the interest in this material has been huge. Material scientists, working in the coal, steel, and nuclear industry, had observed hollow nanometer-sized carbon filament well before 1991 [2]. They however lacked high-resolution electron microscopy, making it impossible to determine the nanotube structure. Also, the aim of their work was often to prevent growth of these filaments since they were inhibiting their industrial processes.

Theoretical modelling predicted CNTs to have extraordinary properties, which later have been demonstrated experimentally [3]. Looking at the mechanical properties their Young's modulus has been measured to be about 1 TPa [4], which is 5 times stiffer than steel. Their tensile strength has also been measured and was found to be as high as 150 GPa [5], well exceeding the strength of macroscopical materials. Translating these properties to the macroscopic world, a wire having the size of a human hair could lift a weight of 100 kg. Their density is also low, compared to other materials having high Young's modulus and tensile strength, making their specific modulus and strengths
1. INTRODUCTION

even larger in comparison to these materials. In addition, CNTs are also very elastic, and they can be stretched and bent severely without obtaining permanent damage. This makes CNTs attractive to use as a fiber composite in future lightweight, high stiffness and strength materials. Though their mechanical properties have not been fully exploited yet, there are CNT containing products available today, e.g. skis, ice hockey sticks, and surf-boards [6].

It has been observed that SWCNTs buckle when bent, much like a straw would, and this buckling was shown to be reversible, i.e. no permanent damage could be observed when straightening the tube. MWCNTs behave differently during bending, since the inner tubes act as a support for the outer tubes, preventing them from buckling. Instead of a single localized collapse, it develops into a distributed pattern of ripples, along the contracted side of the bent CNT (shown in Fig. 1.1). This phenomenon is referred to as the rippling mode. Modelling of this mode has indicated a decrease in the bending stiffness following the rippling onset [7], which would have implications for future applications.

![Image of modelled 40-walled MWCNT, experiencing rippling. The bending curvature is increased from the topmost to the bottommost tube. Reprinted with permission from [7]. © 2008 Elsevier.](image)

Synthesizing methods can be engineered to obtain vertically aligned carbon nanofibers (VACNFs) having a cup-stacked structure, rather than the concentric cylinder structure of CNTs. These fibers are grown from pre-patterned catalyst particles and could find use in future nanoelectromechanical systems (NEMS), where their bending stiffness is one of the most important parameters.
Measuring the mechanical properties of individual CNTs and VACNFs is challenging because of the small displacements and forces involved. Until recently most reported studies on the mechanical properties of individual CNTs have been theoretical modelling, and the experimental studies are still in a stage of infancy. In this work we have used a recently developed instrument that operates inside an electron microscope and is able to measure forces on the nanoscale \[8, 9\]. The instrument effectively joins atomic force microscopy (AFM) with electron microscopy. This enables direct force measurements on individual free-standing MWCNTs and VACNFs. We can thereby detect the very onset of rippling and study the change in bending stiffness following the rippling onset.

We have found that highly crystalline MWCNTs, grown by arc-discharge, possessed a Young’s modulus close to \(E = 1\) TPa. CVD-grown MWCNT had a one order of magnitude smaller \(E\), whereas the \(E\) of VACNFs where yet another order of magnitude smaller. The smaller Young’s moduli of CVD-grown MWCNTs and VACNFs stems from defects and structural differences. Our results also showed that the rippling starts at very low curvatures and small diameter tubes had a rippling onset at higher strains compared to large diameter tubes. Also, tubes with a larger defect density had a larger critical strain and a larger relative post-rippling stiffness compared to tubes with a smaller defect density. However, the stiffness prior to rippling of the tubes with a large defect density were much lower. We also found that tubes with a larger normalized thickness had a larger critical strain as the inner tubes stabilized the outermost tube against rippling. We also observed irreversible structural changes of MWCNTs bent well past the rippling onset. The findings of this work will have implications for the design of future NEMS applications.
1. INTRODUCTION
Chapter 2

Background

2.1 History

"Carbon nanotubes (CNTs) were first discovered in 1991 by Iijima [1]" is a common phrase found in a manuscript concerning CNTs. There is however a debate regarding who should be credited for the discovery of carbon nanotubes [2]. Filamentous growth of carbon from thermal decomposition of gaseous hydrocarbon had been suggested over 100 years before the famous paper by Iijima. At that time no microscope was able to resolve details smaller than a few micrometers. With the invention of transmission electron microscopy (TEM) details on the nanoscale could be imaged and in 1952 a Soviet Union research group published a paper showing TEM micrographs of hollow tubular carbon filaments with a diameter in the range of 50 nm [10], most probably the first TEM images of a multi-walled CNT (MWCNT). Being the first to publish such images, the authors of [2] claim that Radushkevich and Lukyanovich should be credited for the discovery of CNTs. But the paper by Radushkevich and Lukyanovich did not spark any major interest. For this there are many reasons. Firstly the paper was published in a journal not easily accessible outside the Soviet Union. Also the research on this topic was performed in order to prevent the growth of such filaments in steel industry processing and in the coolant channels of nuclear reactors.

Iijima’s paper was published in Nature, a journal read by a broad scientific public. It was published in a time when the interest in carbon from fundamental physicists was big, following the discovery of the C_60 molecule in 1985 [11], a work that was awarded with the Nobel prize in chemistry in 1996. All of these circumstances contributed to
2. BACKGROUND

the big impact the paper have had. In the paper TEM images and diffraction patterns of individual MWCNTs were published along with a description of their concentric cylinder structure of graphene layers. Two years later Iijima and Ichihashi [12] and another group, Bethune et al. [13], published two independent papers showing the first TEM images of single-walled carbon nanotubes (SWCNTs), further increasing the interest in CNTs.

2.2 Carbon structures

A free carbon atom has the electron configuration 1s^22s^22p^2, where the energy difference between the 2s and 2p orbitals is comparatively small. The small difference enables the wavefunctions of these orbitals to mix when binding to other atoms, thereby increasing the binding energy. Mixing of the orbitals forms new basis sets called hybridizations that are then filled with electrons. When one 2s state mixes with n 2p states it is called sp^n hybridization, where n = 1, 2, 3. Carbon atoms bound together with a sp^1 hybridization will form a 1D chain structure with two electrons in two σ bonds and two electrons in two π bonds per atom. When carbon binds with a sp^2 hybridization three electrons will form three σ bonds and one electron will form one π bond. In sp^3 hybridization all four valence electrons will contribute to four σ bonds. The σ bonds are strong and localized, whereas the π bonds are weaker and less localized. This means that electrons in π and π* bonds can move between the atoms while electrons in a σ bond are fixed at one atom.

Diamond is an allotrope of carbon where the atoms have sp^3 bonds, giving diamond its exceptional physical properties. Diamond is the hardest material known, with an extremely high thermal conductivity. It also has a large bandgap (5.5 eV), making it an electrical insulator and transparent to visible light. Graphite is another allotrope with the difference that the atoms have sp^2 bonds, making graphite a layered material. The atoms are arranged in a honeycomb patterned, forming atomic planes that can be stacked in a hexagonal (ABAB), rhombohedral (ABCABC) or in a turbostratic (randomly stacked) fashion. The inter-planar distance depends on the stacking. Hexagonal and turbostratic graphite have the smallest (3.354 Å) and largest (3.440 Å) inter-planar distance respectively.
In the planes the atoms have $\sigma$ and $\pi$ bonds, while between the planes there are only van der Waals forces, resulting in a very anisotropic material. The intraplane electrical and thermal conductivities are high whereas the interplane counterparts are low. It is similar with the mechanical properties, where the stiffness and strength within a plane are high but very low between the planes. This allows graphite planes to slide past each other easily, making graphite a useful solid lubricant. These mechanical properties are also made use of when writing with a pencil, where graphite layers are easily stripped from the pencil and attached to the paper.

Another allotrope is graphene, for which the demonstration and characterisation of [14] was awarded the Nobel in physics prize in 2010. Novoselov and Geim also exploited the weak bond between graphite layers when obtaining their graphene flakes. Starting with platelets of highly-oriented pyrolytic graphite they peeled of graphene flakes simply using scotch tape. The flakes were characterized showing that graphene is a 2D semimetal, stable under ambient conditions (previously believed to be impossible) [14]. Graphene is a 2D material with extraordinary properties and has since the discovery sparked an enormous interest, partly because of its similarity to carbon nanotubes.

2.3 Structure of CNTs

As stated previously MWCNT are concentric cylinders of graphene and the structure suggested by Iijima in 1991 [1] has later been confirmed and is often described using the chiral vector, $C$:

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2$$  \hspace{1cm} (2.1)

where $n$ and $m$ are two integers and $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors of the hexagonal lattice of the graphene sheet. The chiral vector expresses how the graphene sheet is rolled up to form a SWCNT, and the length of $\vec{C}$ is the perimeter. Depending on the integers $n$ and $m$ a CNT can have various chiralities expressed as $(n,m)$, i.e. rolled up in different ways. The unit vectors, and how they are used to roll up a SWCNT, are shown in Fig. 2.1 (a) where the chiral vector of a (4,3) SWCNT is shown. There are three distinct types of chiralities: armchair with $n = m$, zigzag with $m = 0$, and chiral with arbitrary values of $n$ and $m$. Examples of these three types are shown in Fig. 2.1 (b).
2. BACKGROUND

Figure 2.1: (a) the unite vectors, \( \hat{a}_1 \) and \( \hat{a}_2 \), in a graphene lattice. (b) three types of SWCNT from top to bottom: armchair (5,5), zigzag (9,0), and chiral (7,3). (c) MWCNT constituting of three chiral tubes.

From \( \hat{C} \) the diameter can be obtained and it is given by:

\[
d = \frac{\sqrt{3}}{\pi} a_{C-C} \left( m^2 + mn + n^2 \right)^{1/2}
\]  

where \( a_{C-C} \) is the bond length between the carbon atoms in graphene (1.42 Å). It should be noted that Eq. 2.2 yields the diameter of a circle going through the atomic positions and do not take the size of the carbon atoms into account. The wall thickness of a SWCNT is often defined to be around 0.34 nm, i.e. the interplanar spacing in graphite. From this definition the outer diameter, \( d_o \), of a SWCNT with a diameter, \( d \), given by Eq. 2.2 would be \( d_o = d + 0.34 \) nm. In the same sense the inner diameter would be \( d_i = d - 0.34 \) nm, hence yielding a wall thickness of 0.34 nm.

As mentioned earlier there are also multiwalled carbon nanotubes, consisting of multiple concentric cylinder with a spacing similar to the interplanar spacing in turbostratic graphite (3.440 Å). An example of a MWCNT is shown in Fig. 2.1 (c) where three concentric chiral CNTs constitute a MWCNT. For a more thorough description of the structure see for example [3].
2.4 Properties

2.4.1 Electronic properties

Soon after the “discovery” of MWCNT in 1991, theoreticians began calculating the electronic structure for the simplified case of SWCNTs. From calculations it was found that the electronic structure depended on the chirality, \((n,m)\). CNTs with chirality satisfying the condition:

\[ n - m = 3j \]  \hspace{1cm} (2.3)

where \(j = 0, 1, 2, \ldots\) were found to be metallic while the CNTs not satisfying the relation were found to be semiconducting [15]. The dependence of the electronic structure on the chirality can be understood by looking at what happens when graphene is folded into a CNT. Graphene is a zero-gap semiconductor where the occupied \(\pi\) band and the unoccupied \(\pi^*\) band meet at Fermi level at the \(K\) point in the Brillouin zone. When folding graphene into a CNT, periodic boundary conditions in the circumferential direction are imposed, resulting in exclusion of many \(k\) states. The \(K\) points are excluded if Eq. 2.3 is not satisfied, hence resulting in a semiconducting CNT. These calculations were later verified by performing scanning tunneling spectroscopy on individual SWCNT [16, 17].

Because of their perfect crystal symmetry, SWCNT also act as quantum wires with ballistic conductance and can withstand high current densities [18]. These electronic properties make CNTs an interesting material for future electronic applications.

The extraordinary properties presented above are only present in straight and perfectly crystalline CNTs. Defects and local structural changes, such as kinks induced from bending, will affect these properties. Studies have shown that the conductance will decrease when bending causes kinks in SWCNTs [19, 20, 21, 22]. At the kinks the \(sp^2\)-orbitals become rehybridized, which changes the electronic structure and lowers the conductance. Knowledge about when such kinks are created and how they affect the properties of the nanotube is therefore of great importance.

2.4.2 Mechanical properties

The \(sp^2\) bond does not only give CNTs fascinating electrical properties, it is also one of the strongest and stiffest chemical bonds in an extended system known in nature [23]. As for the stiffness, the in plane elastic constant, \(c_{11}\), of graphite was at the "discovery"
2. BACKGROUND

of CNTs known to be 1.06±0.02 TPa \cite{24}, almost five times that of steel. Since graphite and CNTs both have sp$^2$ bonding, the mechanical properties of CNTs were predicted to be similar to graphites.

Early theoretical work on the mechanical properties focused on the strain energy per atom \cite{25}. From molecular dynamics, using empirical potentials, it was found that the strain energy increased with decreasing diameter, while approaching the values for graphite at large diameters. This result agrees with the classical result saying that $E_{\text{strain}} \propto 1/d^2$. In the same work, the stiffness of several SWCNTs was calculated and it was found to be close to $c_{11}$ of graphite.

Measurements of the mechanical properties on macroscopical materials are often made by mounting a standard specimen of the desired material in an instrument that exerts deformations on the specimen and measures the resulting forces. This becomes difficult for materials on the nanoscale because of the small dimensions. Other methods are therefore needed to determine the mechanical properties of CNTs. An early experimental estimation of the stiffness of MWCNTs was made by looking at the amplitude of their intrinsic thermal vibrations inside a TEM. By assuming the MWCNTs to be cantilevered beams with a circular cross section they obtained a Young's modulus, $E$, varying between 0.40-4.15 TPa \cite{26}. The same group later published another paper where they had improved their method and looked solely on SWCNTs where they found $E = 1.25^{+0.45}_{-0.35}$ TPa, by using a layer thickness of 0.34 nm \cite{27}. These studies, though having large uncertainty, show the high stiffness of CNTs. However, they do not describe how CNTs will respond to applied loads in an application.

Another study used MWCNTs lying on a substrate, clamped at one end and deflected at the other end with an AFM cantilever. This yielded a force-displacement, $F - \delta$, curve, telling how the cantilevered MWCNTs responded to the bending. From these $F - \delta$ curves the spring constant could be obtained, and together with the outer diameter and length of the MWCNTs, used to calculate Young's modulus. Their obtained Young's modulus was $E = 1.28 \pm 0.5$ TPa \cite{28}. In addition to this they also saw that MWCNTs could be bent to large curvatures without any irreversible deformation, i.e. withstand large deformation elastically. However, at a certain deflection they saw a kink in the $F - \delta$ curves, after which the spring constant appeared to have decreased. Imaging MWCNTs bent above this deflection revealed a change in topology, where bumps showed up on the cylinder surface. Changes in the internal structure have also
been observed in a TEM study of MWCNTs where tubes were statically bent during the sample preparations, and showed signs of buckling [29].

The buckling was further investigated in another TEM study accompanied by molecular dynamics (MD) simulations [30]. The simulations were performed to study the behaviour of bent CNTs and reproduced the buckling pattern for a SWCNT and a DWCNT. They also showed that the strain energy of the CNTs increased linearly when bent past the critical curvature for buckling, equivalent of continuing deformation under a constant force. Another MD study showed similar behaviour of CNTs subjected to bending, and also showed morphology changes of CNTs subjected to twisting and axial compression [31]. This non-linear elastic behaviour allows CNTs to withstand large deformations without any irreversible deformation. Studies on the mechanical properties of CNTs will be discussed further in Section 2.4.2.1 and 2.4.2.2 where experimental and theoretical studies are presented respectively.

2.4.2.1 Experimental

As discussed in section 2.4.2 CNTs have extraordinary mechanical properties, but because of their small dimensions the characterization of these properties is difficult. This section summarizes different methods that have been used to characterize the mechanical properties of CNTs.

In the earliest article reporting measurements of the Young’s modulus, $E$, the authors looked at the thermal vibrations and assumed the CNTs to be equivalent to a cantilevered homogeneous cylindrical beam [26]. They showed that the amplitude of the thermal vibrations, $\sigma$, of the free end of a cantilevered cylindrical beam is given by:

$$\sigma^2 = \frac{16l^3k_B T}{\pi E(r_o^4 - r_i^4)} \sum_n \beta_n^{-4} \approx 0.4243 \frac{l^3k_B T}{E(r_o^4 - r_i^4)}$$

(2.4)

where $l$, $r_o$, and $r_i$ is the length, outer radius and inner radius respectively, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\beta_n$ is a constant for the free vibration of mode $n$. By studying bundles of CNTs in a TEM they found isolated CNTs protruding from the bundle. The amplitude of the vibrations of the free ends was estimated along with the dimensions of the CNTs and used in Eq. 2.4, resulting in $E = 0.4 - 4.15$ TPa. The big uncertainty stems from the difficulty in determining the amplitude of the vibrations and the length of the CNTs. Another uncertainty is the value of $T$
2. BACKGROUND

which was assumed to be around room temperature, as measured by a thermocouple close to the sample. The electron beam of the TEM will locally heat up the specimen, thus raising $T$ of the CNT above room temperature. Using a lower $T$ than the true will underestimate the value of $E$ according to Eq. 2.4. The authors estimated the local heating in a later publication to be $\Delta T = 20 - 40^\circ C$, which would shift all their values of $E$ towards higher values by about 10%. This method, with improved ways for determining $\sigma$ and $l$, has also been used to estimate $E$ of SWCNTs. Assuming the SWCNT to be hollow cylinders with a wall thickness of 0.34 nm a Young’s modulus of $E = 1.25^{+0.45}_{-0.35}$ TPa was found \[27\].

Another method also assumed CNTs were cylindrical cantilevers, but instead of looking at their vibrations, individual CNTs were bent with an AFM cantilever \[28\] (for the geometry see Fig. 2.2 (a)). CNTs were clamped by first depositing CNTs on a MoS$_2$ single crystal surface. In the next step pads of a rigid oxide, SiO, was deposited through a shadow mask. AFM was then used to locate CNTs having a nice geometry and being pinned by a pad. These CNTs were then pushed sideways resulting in $F$-$\delta$ curves. Using the slope of this curve, the spring constant, $k$, of the CNTs could be determined. Along with the CNT dimensions the Young’s modulus could also be determined using the equation from beam theory:

$$E = \frac{4kl^3}{3\pi r_o^4}$$ (2.5)

where $l$ is the length from the point of attachment to the point of the applied force. Using this method an average value of $E = 1.28 \pm 0.59$ TPa was obtained. Another interesting feature was discovered in the $F$-$\delta$ curves, namely a non-linear $F$-$\delta$ relation \[28\]. At a certain deflection the spring constant of the CNT drastically decreased but continued to be linear (or close to). Bumps on the CNTs could be imaged on severely bent CNTs suggesting that the CNTs had buckled, thus causing the change in spring constant. These images were acquired by using a high-friction surface, keeping the CNT bent after it was released by the AFM-tip. Relaxing these CNTs and imaging them again showed no signs of irreversible deformation. Also their $F$-$\delta$ behaviour was unaltered after the buckling suggesting this phenomena to be reversible. Other AFM studies have also shown that CNTs can withstand large bending curvatures reversibly \[32, 33\].
2.4 Properties

This behaviour was also seen in a TEM study where static and dynamic mechanical deflections were electrically induced in cantilevered MWCNTs [4]. This was done by first attaching carbon soot containing MWCNTs to a fine gold wire. The wire was then mounted on a piezoelectrically driven translation stage, enabling fine movement of the sample. A potential could also be applied to the sample, and in close proximity, 5-20 μm, a counter electrode was placed. When a potential was applied between the stage and the counter electrode the CNTs became electrically charged and were attracted to the counter electrode. By studying the bending of the CNTs, the charge appeared to be localized at the tip of the CNTs. When applying a time-dependent potential between the stage and the counter electrode, the CNTs began to oscillate. By varying the frequency of the time-dependent potential the eigenfrequency of the CNTs could be obtained. From beam theory it is known that the eigenfrequency of mode *n* of a cantilevered cylindrical beam is given by:

\[
\nu_n = \frac{\beta_n^2}{8\pi^2} \sqrt{\frac{d_o^4 - d_i^4}{E \rho l}}
\]

where \(\beta_n\) is the constant for the free vibration of mode \(n\), \(l\) is the length of the beam, \(d_o\) and \(d_i\) is the outer- and inner-diameter respectively, \(E\) the Young’s modulus, and \(\rho\) is the density. By finding the eigenfrequency of the first mode, \(\nu_1\), and using \(\beta_1 = 1.875\) along with the CNT dimensions, \(E\) could be extracted. Using this method the authors found values for Young’s modulus varying between 1.3-0.1 TPa, where \(E\) seemed to decrease with increasing diameter. The authors explained this decrease with the emergence of another bending mode, which appears in CNTs bent at large curvatures. On the contracted part of the bent CNT a wavelike pattern of ripples was clearly seen in their TEM images. Another work also showed TEM images of this rippling pattern, where MWCNTs embedded in a polymer were studied. MWCNTs bent to high curvatures by the polymer matrix showed that the rippling pattern extended over large regions without any collapse of the MWCNTs [34].

AFM measurements were used in another study where droplets of a suspension containing CNTs were deposited on a well-polished alumina ultrafiltration membrane [35]. This membrane had pores with a diameter of ~200 nm. AFM was then used to find CNTs with part of its length lying across a pore, but with most of its length being in contact with the membrane surface. CNTs fulfilling this were strongly attached to
2. BACKGROUND

the membrane surface and the part lying across a pore was assumed to be similar to suspended beams with circular cross-sections, see Fig. 2.2 (b) for the geometry.

![Figure 2.2: (a) Cantilevered beam and (b) suspended beam exposed to a point load, \( F \).](image)

From beam theory, the deflection, \( \delta(x) \), of the beam can be found. The magnitude of \( \delta \) depends on the \( E \) and the dimensions of the beam.

By deflecting the CNT by a distance \( \delta \) with the AFM cantilever at half of the suspended length while measuring the resulting force, \( F \), the Young’s modulus was obtained using the \( F-\delta \) relation from beam theory:

\[
\delta = \frac{Fl^3}{3\pi E(d^4 - d^4_i)}
\]

In their work the authors studied three different sorts of MWCNTs: arc-discharge grown, annealed arc-discharge grown, and catalytic chemical vapour deposition (CCVD) grown. The annealed arc-discharge grown MWCNTs were heated to 2500\(^\circ\)C, aiming at reducing point defects. Structure disorder is known to be present in a larger extent in CCVD grown tubes, which is why these tubes were used. The study showed no apparent effect of the annealing, since the annealed arc-discharge grown tubes actually had a smaller mean Young’s modulus (\( E_{\text{annealed}} = 755 \) GPa compared to \( E_{\text{as\,-\,grown}} = 870 \) GPa), while \( E \) for CCVD grown tubes was almost two orders of magnitude smaller with a mean value of \( E_{\text{CCVD}} = 27 \) GPa. The authors explained the small values of \( E_{\text{CCVD}} \) with the structure disorder in the CCVD grown tubes, where this disorder made the walls of the MWCNT non-parallel to the tube axis. The structure of these tubes can be approximated with the cup-stacked structure, seen in Fig. 2.3 (a), where cups of graphene are stacked in one another.

Deviation of the angle \( \theta \) from \( 0^\circ \) enables gliding of the planes, and the weak van der Waals force between the layers begin to dominate the deformation. For a single crystal
of graphite, and other transversely isotropic materials, the Young’s modulus depends on the angle $\theta$ as [35]:

$$\frac{1}{E} = s_{11}(1 - \sin^2 \theta)^2 + s_{33}\sin^4 \theta + (2s_{13} + s_{44})\sin^2 \theta(1 - \sin^2 \theta)$$  \hspace{1cm} (2.8)

where $s_{ij}$ are the elastic compliances of the material. For graphite, reported values of $s_{44}$ are in the range of $200 \leq s_{44} \leq 5000 \text{TPa}^{-1}$, although most reported values are close to $s_{44} = 5000 \text{TPa}^{-1}$.[36] Other values of the elastic compliances are $s_{11} = 0.98 \text{TPa}^{-1}$, $s_{33} = 27.5 \text{TPa}^{-1}$, and $s_{13} = -0.33 \text{TPa}^{-1}$.[24] Thus independently of its exact value, $s_{44}$ is much larger than the other elastic compliances and the Young’s modulus is thereby significantly lowered as $\theta$ deviates from zero. Using the values of $s_{11}$, $s_{33}$, $s_{13}$ and the two extreme values of $s_{44}$, Eq. 2.8 is plotted and shown in Fig. 2.4. From this plot it is clear that the Young’s modulus drops dramatically even for small $\theta$.

![Figure 2.3](image)

**Figure 2.3:** (a) Cup-stacked structure in comparison with (b) the concentric cylinder structure.

![Figure 2.4](image)

**Figure 2.4:** Dependence of the axial Young’s modulus on the angle of the graphene planes, according to Eq. 2.8, for two extreme values of $s_{44}$.

In similar studies the same group later reported low values of Young’s modulus
(10 < E < 100 GPa) for CVD grown CNTs appearing to have concentric cylinder structure [37, 38]. They explain the low values of E with the introduction of structural defects during growth. The exact role and mechanics of these defects are unknown but the authors propose a model of a series of high-quality segments joined by poorly connected nodes [38].

2.4.2.2 Theoretical

Because of the difficulties in controlling and measuring the boundary conditions, the forces, and the displacements of CNTs experimentally, most studies trying to characterize the non-linear behaviour of CNTs have been performed theoretically. The earliest report used molecular dynamics (MD) to model buckling of SWCNTs and DWCNTs [30]. A similar study also used MD, and compared the results to a continuum shell model [31]. They found good agreement between the continuum approach and the MD simulations, and proposed the use of an extended continuum model to study multi-walled tubes. Using MD to study MWCNTs becomes very computationally expensive as the number of walls is increased. Therefore other approaches are also used to model deformation behaviours of MWCNTs.

A refined version of the continuum approach was developed where each individual tube in a MWCNT was modelled as an elastic shell. Each shell was given an effective thickness, \( h \), an effective Young’s modulus, \( E_{\text{eff}} \), and a Poisson’s ratio, \( \nu \), similar to the ones described in [31]. From these properties the flexural rigidity, \( D \), and the in-plane stiffness, \( C \), of a shell can be calculated using:

\[
D = \frac{E_{\text{eff}}h^3}{12(1-\nu^2)} \tag{2.9}
\]

and

\[
C = E_{\text{eff}}h \tag{2.10}
\]

In addition, each shell was ascribed with an excess internal strain energy, because of the curvature of the tube, assumed to depend on the diameter as \( 1/d^2 \). The wall spacing was set to 0.34 nm, and the van der Waals interactions between the walls was modelled with a Lennard-Jones potential while the shear was assumed to be zero. Using this model, finite element method (FEM) simulations showed a rippling pattern similar to the patterns observed experimentally [4, 28, 29, 39] in bent tubes. They also found
that the moment-curvature, $M - \kappa$, dependence was initially linear but changed at the rippling onset. After the rippling onset the $M - \kappa$ relation is non-linear as the rippling spreads to the inner tubes. When all tubes are rippled the $M - \kappa$ relation continues to be linear albeit with a smaller spring constant than prior to the rippling.

Modelling the graphene walls as elastic shells works well at small deformations. However, after the rippling onset the graphene walls are largely deformed and the walls will deform non-linearly, the linear shell model then has difficulties in describing this behaviour. Ultimately the simulations should be done using MD, where contributions from each atom are used to determine the behaviour of the MWCNT, but this becomes too computationally expensive. To account for the non-linear mechanical behaviour of the graphene walls one research group used the Green strain tensor to describe the mechanical properties \[40\]. However their use of the Green strain tensor only permitted them to use flat atomic layers, whereby they modelled the MWCNT as a rectangular beam with the graphite planes being parallel to the axis and perpendicular to the bending plane. Modelling this structure under pure bending using FEM, the authors found a $M - \kappa$ behaviour they fitted to a bi-linear relation. They also found that the spring constant decreased by a factor of 2, after the rippling onset, and that it starts to ripple at a critical strain of $\epsilon_{cr} = 0.006$. 

In another approach \[41\] the mechanical properties of the graphene walls were systematically inherited from the Brenner atomistic potential. This potential is ascribed to 2D objects in a FEM simulations, thereby not requiring any artificial thickness of the layers. Inheriting the atomic potential includes the non-linear mechanical properties of graphene into the model without increasing the degrees of freedom too much, enabling simulations of thick MWCNTs. This potential also includes the internal strain energy of the walls depending on the diameter as $1/d^2$. The inter-wall van der Waals interaction was modelled using a Lennard-Jones potential. Using this model the authors modelled MWCNTs exposed to pure bending and twisting and found the rippling patterns for both loading conditions. In bending they initially found a linear $M - \kappa$ relation and after the rippling onset the relation followed $M \propto \kappa^n$ with $0 < n < 1$. The critical strain for the rippling onset was found to depend on the outer radius of the MWCNT as $\epsilon_{cr} = 0.1/r$. This contradicts the result of \[40\], where a constant $\epsilon_{cr}$ was predicted.

A similar dependence of $\epsilon_{cr}$ on $r$, as in \[41\], was found by a group using MD to simulate the mechanical behaviour of MWCNT \[42\]. By only using armchair type CNTs
they could employ periodic boundary conditions and thereby reduce the number of atoms used in their model to less than 1920. Using only armchair CNTs is a reasonable assumption since earlier reports have shown that the mechanical properties are insensitive to the chirality. The authors used the Tersoff and the Lennard-Jones potential to model the intra-tube and inter-tube interactions respectively. They found that the critical strain depends on the radius as $\varepsilon_{cr} = 0.05/r$, i.e. a similar dependence as in [41]. They also found a nearly linear post-rippling $M - \kappa$ relation albeit with a lower spring constant after the rippling onset. The ratio between the spring constants after and before rippling, $k_r/k_i$, was found to depend on the number of walls ranging from 0.15 and converging to 0.65 for MWCNTs with more walls.

All the models discussed above assumed perfect MWCNT with no defects. In a recent study, the model [41] was extended so that the influence of different defects on the mechanical properties was studied [43]. In addition to the intra-plane inherited Brenner potential and the inter-plane Lennard-Jones potential, $sp^3$ and $sp^2$ defects between the layers were modelled as tensional and shear spring constants. Using a defect density, $\rho$, the authors homogenized the potential energy of these defects, thereby enabling a continuum description. The $sp^3$ defects were modelled as interstitial carbon atoms linking two adjacent walls together, while the $sp^2$ defects were modelled as single-atom vacancies in adjacent walls forming a bond. When performing pure bending simulations on identical MWCNTs with varying defect densities the authors found that $\varepsilon_{cr}$ increased linearly with $\rho$. They also found that the post-rippling stiffness increased linearly with $\rho$ for $sp^3$ defects and close to linearly for $sp^2$ defects. However the introduction of $sp^2$ defects also lowered the pre-rippling stiffness, while it was unaffected for the $sp^3$ defects.
2.5 Applications

2.5.1 Electrical

Many potential applications of CNTs have been proposed as a result of their remarkable properties. Individual metallic SWCNTs have been proposed to function as interconnects for integrated circuits because of their small size, ballistic transport and ability to withstand high current densities [18]. Semiconducting SWCNTs can in turn be used as the channel material in field effect transistors [44]. Devices employing SWCNTs as interconnects and channel material could be smaller, faster and more energy efficient than today’s silicon-based devices. However, before having large integrated circuits consisting of SWCNTs, techniques for depositing or growing SWCNTs, with a predefined chirality, are needed [45]. The electronic properties have been exploited to fabricate thin, flexible, and transparent films of SWCNTs [46]. Although bulk samples of CNTs are one of the darkest materials known [47], thin films can have a high transparency. The electrical conduction of these films show little degradation after repeated strain cycles, making them an attractive material to use as transparent electrodes in flexible photovoltaic devices [46].

2.5.2 Mechanical

Because of their high stiffness and yield strength together with their low weight, incorporation of CNTs in various matrices has been studied. These composites often show an increase in stiffness and strength but they are far from the properties of individual CNTs [48]. Before one can obtain composites that fully exploits the mechanical properties of CNTs, the bonding between CNTs and the matrix as well as the alignment and dispersion of CNTs in the matrix needs to be improved. These are difficult tasks because of the small dimensions and tendency to bundling of several CNTs through van der Waals forces. Though their mechanical properties have not yet been fully exploited, there are CNT containing products available today, e.g. skis, ice hockey sticks, and surf-boards [6]. The addition of CNTs to these composites mainly increase their strength and toughness, but it can also increase the stiffness.
2. BACKGROUND

2.5.3 Nanoelectromechanical systems

It has been shown that CNTs cantilevered to an electrode will bend towards a counter electrode when a potential is applied between the electrodes, due to an electrostatic force\[^4\]. This phenomenon was used to excite the eigenfrequency of the CNTs. Using this frequency, along with the CNT dimensions, the Young’s modulus could be calculated (described in more detail in section 2.4.2). Because of their small size, low weight, high stiffness, and high electrical conductance it was early proposed to exploit this phenomenon in nanoelectromechanical systems (NEMS). The high stiffness of a clamped CNT enables high operating frequencies since the eigenfrequency, \( \omega \), of a clamped beam is given by:

\[
\omega = B \sqrt{\frac{EI}{\rho Al^4}} \tag{2.11}
\]

where \( B \) is a constant depending on the boundary conditions, \( I \) is the moment of inertia, \( \rho \) the density, \( A \) the cross-sectional area, and \( l \) the length of the beam. Cantilevered CNTs can have eigenfrequencies in the gigahertz range, making them an ideal candidate in nanoelectromechanical switching devices\[^49\].

Several NEMS exploiting the electrostatic bending of CNTs have been proposed. In an early article the threshold voltage for a two-terminal switch employing a CNT was studied. Their geometry consisted of a CNT cantilevered to an electrode that was attracted to form a closed circuit to a counter electrode\[^50\]. Though they found low threshold voltages, these voltages would induce large currents in the CNT, in closed circuit. These high currents were avoided in another geometry where an additional gate electrode was used\[^51\]. In this proposed model, pictured in Fig. 2.5 (a), a relatively high voltage is applied between the source (S) and gate (G) electrodes, causing the CNT to bend towards the drain (D) electrode. The source-drain voltage can in this geometry be held relatively low. This model has been further studied and demonstrated\[^52, 53, 54, 55\], though not reaching the predicted gigahertz switching frequencies for various reasons.

In another approach vertically aligned CNTs, as pictured in Fig. 2.5 (b), where used to form a switch. The advantage of using this geometry is that vertically aligned CNTs can be grown from patterned catalysts, simplifying the device production. In this model a large source-gate voltage is applied causing the drain CNT to bend towards the source CNT, while a smaller source-drain voltage is maintained. This device was
demonstrated in [56] and further refined by the same group in [57]. Since then research has been made aiming further simplifying the fabrication of these devices [58, 59].

Other NEMS using the electrostatic bending of CNTs include: double clamped switches [60, 61, 62], atomic-resolution mass sensor [63], and nanotube radio [64] to mention a few.

![Figure 2.5](image-url)

Figure 2.5: (a) Nanorelay build up by three electrodes and a CNT on an insulating substrate. By applying a source-gate voltage the CNT is attracted towards the gate and drain electrode [51]. (b) Nanoswitch employing two CNTs and three electrodes. By applying a large voltage, of the same sign as the drain electrode, to the gate electrode the drain CNT will bend towards the source CNT [57].

Modelling of the CNTs and CNFs in the applications described above were made by assuming them to be linear elastic beams with a Young’s modulus of $\sim 1$ TPa. However, only defect free CNTs, produced using high temperature methods, show a Young’s modulus of 1 TPa, while CNTs grown using catalytic low temperature methods can show Young’s moduli two orders of magnitude smaller [35]. It has also been reported that CNTs behave non-linearly when bent at large curvatures, reducing their stiffness [4]. Therefore it is important to characterize the mechanical properties of the materials proposed to be used in future NEMS applications.
2. BACKGROUND
Chapter 3

Experimental

3.1 Electron microscopy

An optical microscope cannot resolve objects with dimensions on the nanoscale since their resolution is limited by the wavelength of the light (>300 nm). When de Broglie in 1925 showed that electrons also possessed wave-like characteristics it was suggested that electrons could be used in microscopes instead of light. The advantage is that the wavelength of electrons is inversely proportional to the square root of their energy, e.g. an electron accelerated through a voltage of $V_{acc} = 100$ kV has a wavelength of $\lambda \approx 4$ pm. Theoretically this enables a subatomic resolution if the lenses in the microscope would be perfect. However, electromagnetic lenses suffer from a number of aberrations that decreases the theoretical resolution to $\sim 1$ Å (aberration corrected TEM have even higher resolution).

The first electron microscope was a TEM and was built by Ruska and Knoll in 1932, an achievement which was awarded the Nobel prize in 1986. A TEM works like a slide projector in a sense that a broad parallel beam of electrons (light) are passed through an electron transparent sample (slide) and the transmitted intensity can be viewed on a fluorescent screen (projection). More on how a TEM works is described in section 3.3. The first SEM was built in 1937 by von Ardenne. An SEM image is obtained by scanning, pixel-by-pixel, a focused electron beam over an electrical conducting sample and collecting the secondary electrons. In a SEM, bulk specimen can be examined while TEM specimen needs to be very thin to be transparent to electrons, and small enough to fit inside the objective lens.
3. EXPERIMENTAL

Common for the two microscopy techniques are the electron gun and the electromagnetic lenses which are described below. After these two subsections a more detailed description of the two techniques is given.

3.1.1 Electron gun

The purpose of the electron gun is to supply the microscope with free electrons accelerated by a voltage, $V_{acc}$. Electrons are obtained from a source by overcoming the source materials work function. This can be done by either heating the source (thermionic emission) or by applying a large local electric field at the source (field emission) or by a combination of these two. Thermionic emission guns often consist of a tungsten wire bent into a V-shape as the cathode, often referred to as a hairpin-filament. There are also other thermionic sources, e.g. the LaB$_6$ cathode which has a lower work function compared to tungsten. The hairpin-filament is heated to a temperature of 2000-2700 K and a voltage applied to the anode extracts electrons from the tip. To reduce the emission at large solid angles, the tungsten cathode is surrounded by a Wehnelt element. This element is biased with a slightly negative voltage and acts to focus the emitted electrons into a beam cross-over. Tungsten filaments can supply large beam currents but this current is emitted from a relatively large area requiring a large demagnification from the electron lenses to achieve a small electron probe at the sample. The axial gun brightness $\beta$, defined as the current $\Delta I$ passing through an area $\Delta A$ into a solid angle $\Delta \Omega$:

$$\beta = \frac{\Delta I}{\Delta A \Delta \Omega}$$  \hspace{1cm} (3.1)

is relatively low for tungsten filaments. The advantages of these filaments are that they are cheap and stable and do not require as high vacuum when operating, as compared to field emission guns.
3.1 Electron microscopy

A field emission gun (FEG) consists of a cathode with a sharp tip ($r_{\text{tip}} < 100$ nm), an anode is used to extract electrons from the cathode and a second anode to accelerate the extracted electrons. The material of the cathode tip is usually single crystal tungsten, because of the dependence of the emitted current on the crystal orientation. Having emittance at large solid angles will cause a lot of electrons to hit the first anode and hence create ions that would be accelerated towards the cathode and damage the source. The (100) direction in tungsten limits the emittance to a cone with a semi-apex angle of about 0.1 rad, thus reducing the probability of electrons hitting the anode. The area from where the electrons are extracted is small compared to a thermionic source. Thereby the need for demagnification of the beam is much smaller. FEG-SEMs routinely gives electron probe sizes of $1 - 5$ nm at the sample, enabling high resolution imaging at low acceleration voltages. The brightness of a FEG is two orders of magnitude larger than that of thermionic sources and they also have longer lifetimes. The disadvantage of FEGs is that they are more expensive and less stable than thermionic sources. They also require higher vacuums during operation, and are usually differentially pumped.

3.1.2 Electromagnetic lenses

After the electron gun the electron beam reaches a number of electromagnetic lenses. The electromagnetic lenses usually consist of a coil of copper wire enclosed by an circular symmetric iron casing, as shown in Fig. 3.1 (a). Applying a current to the coil induces a magnetic field, $\vec{B}$, that focuses off-axis electrons toward the optic axis through the Lorentz force:

$$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B})$$

(3.2)

where $-e$ and $\vec{v}$ is the charge and velocity of the electron respectively and $\vec{E}$ is an electric field. Because of this force, the electrons move in spirals down the column towards the optical axis. The magnetic field from the lens is axially symmetric and increases in strength going away from the optical axis. This results in a larger force for electrons further away from the optical axis. Applying a larger current through the coils will increase the magnetic field, deflecting the electrons more. So by controlling the current through the coils the strength of the lens is controlled. Resistive heating is
caused by the current through the coils, so the lenses need to be cooled by circulating water around them.

Another component in the electron beam column is the stigmator, as shown in Fig. 3.1 (b). A stigmator consist of a number of poles (eight poles in Fig. 3.1 (b)) that applies a weak non-axially symmetric magnetic field aiming at making the beam circular symmetric. A beam that is not circular symmetric will render an astigmatic image that can be recognized by observing how known circular objects appear stretched in one direction, hence distorting the image and reducing the resolution.

Apart from astigmatism the electromagnetic lenses also suffer from a number of other aberrations. Thus they cannot focus the electron beam into a homogeneous spot on the specimen surface, but rather into a disk of least confusion with diameter $d_p$. Spherical aberration occur in the lenses because electrons further away from the optic axis are affected by a stronger magnetic field than electrons closer to the optic axis. This causes electrons further away form the optic axis to be deflected more resulting in a cross-over earlier in the column. This spherical aberration will result in a disk of least confusion having diameter $d_s$, as illustrated in Fig. 3.2.

Not all electrons emitted from the electron gun have the same energy. Because of this energy spread, electrons with a lower energy are focused onto the optic axis earlier in the column. This phenomenon is called chromatic aberration, resulting in a disk of least confusion with diameter $d_c$. Another source of imperfection in the lens system is the apertures. For small apertures the beam electrons are diffracted in a circular way.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{emlens.png}
\caption{Cross sectional schematic of an electromagnetic lens. (b) Top view of a stigmator assembly with eight poles.}
\end{figure}
3.1 Electron microscopy

Figure 3.2: (a) Schematic of a perfect lens where all off-axis electrons are being focused into a spot. (b) Schematic of a lens suffering from spherical aberration where electrons further away from the optic axis are focused earlier onto the optic axis, resulting in a disk of least confusion, with $d = d_s$, instead of a spot.

pattern with diameter $d_d$.

Assuming the distribution of these aberrations to be Gaussian and also adding the demagnified diameter of the electron source, $d_0$, the total diameter of the electron probe can be written as:

$$d_p = (d_0^2 + d_s^2 + d_{a}^2 + d_c^2)^{1/2}$$ (3.3)

The resolution of an SEM can be as good but never better than $d_p$ which will be discussed in more detail later. Modern SEM employing a FEG can obtain probe diameters as small as $d_p = 1$ nm, where the diameter increases with decreasing acceleration voltage.
3. EXPERIMENTAL

3.2 Scanning electron microscopy

An SEM image is obtained by scanning a focused electron beam on a specimen surface, pixel by pixel, and detecting the electrons escaping from this surface. The detected electron intensity, $I(r)$, as a function of the lateral coordinates, $r$, forms an image, usually displayed in gray-scale where white is maximum intensity. In order to obtain a focused electron beam, an SEM needs to have two components: an electron gun and electron lenses. The components are usually positioned with the gun at the top and the lenses below, ending with the sample at the bottom as illustrated in Fig. 3.3. Different detectors at different positions in the SEM are also illustrated in this figure.

![Figure 3.3: Schematic sketch of an SEM. Modified from [67].](image-url)
3.2 Scanning electron microscopy

3.2.1 Beam-specimen interaction

When the beam hits the specimen the electrons will interact with the atoms, consisting of a localized positively charged nuclei and the dispersed negatively charged electrons. Some beam electrons will be scattered elastically at large angles. After a number of such events this can lead to electrons escaping the specimen, retaining much of their initial energy. These electrons are called backscattered electrons (BSE) and have by convention an energy larger than 50 eV. The backscattering coefficient, i.e. how efficiently a material backscatters electrons, is proportional to the square of the atomic number of the specimen, \( Z^2 \).

While travelling through the specimen, the beam electrons will gradually lose energy through inelastic scattering events, giving rise to secondary electrons (SE) and X-rays. The SEs can be used to form an image of the specimen and the X-rays to get elemental analysis of the specimen. Since the loss of energy is gradual, some electrons can travel large distances within the specimen, repeatedly creating SEs and X-rays, before coming to rest. This results in a large information volume for bulk specimen. Thus even if \( d_p \) is small, the information volume is large, reducing the image resolution as illustrated in Fig. 3.4. The energy loss of the beam electrons is proportional to the atomic number, \( Z \), and the distance travelled in the specimen, \( z \).

![Figure 3.4](image)

**Figure 3.4:** The volume reached by the primary electrons (PE) and the origin of different signals. Secondary electrons (SE\(_1\)) generated directly by the PEs that escape the specimen are originating from a small volume close to the surface. Backscattered electrons (BSE) can travel longer distances in the specimen and hence originate from a larger volume. As BSEs travel in the specimen they will create secondary electrons (SE\(_2\)) contributing to the total SE signal. X-rays can travel even larger distances in the specimen and hence have the largest origin volume.
3. EXPERIMENTAL

3.2.2 Beam interaction with carbon nanotubes

For thin specimens of a low atomic number, such as CNTs, the electron beam will penetrate the specimen losing only a negligible amount of energy. Also the probability of backscattering from such specimen is low resulting in a small interaction volume. The majority of the electrons coming from a CNT, as a result of the electron beam, are thus SEs directly generated by the incident beam. In order for these electrons to reach the detector they should not be reabsorbed or scattered in the CNT. The probability of escaping from a specimen decreases with the distance travelled in the solid as:

\[ P_{\text{escape}} \propto e^{-\alpha z} \]  

(3.4)

where \( \alpha \) is the absorption coefficient for SE of the specimen material. Assuming the SE generation to be proportional to the thickness \( t \) and using Eq. 3.4, an expression for the SE yield \( (\delta_t) \) as a function of \( t \), was derived in [68]:

\[ \delta_t \propto \frac{1}{2\alpha} \left( 1 - e^{-\alpha t} (1 - \alpha t) - (\alpha t)^2 \int_{\alpha t}^{\infty} e^{-\xi} \xi d\xi \right) \]  

(3.5)

where the \( t \) is a function of the lateral coordinates, \( t = t(r) \).

The SE yield is also dependent on the tilt angle between the specimen and the electron beam. Defining the tilt angle \( \phi \) as the angle between the surface normal and the beam, the SE yield then depends on \( \phi \) approximately as [69]:

\[ \delta_\phi \propto \sec \phi \]  

(3.6)

where \( \phi \) is a function of the lateral coordinates, \( \phi = \phi(r) \). For materials with low \( Z \) the dependence of \( \delta_\phi \) on \( \phi \) becomes more rapid. However, the dependence becomes slower for lower acceleration voltages, and Eq. 3.6 is a good approximation for CNTs when using low acceleration voltages. Combining Eq. 3.5 and 3.6 gives the total SE yield:

\[ \delta_{\text{sim}}(r) = \delta_t(r) \delta_\phi(r) \]  

(3.7)

From this equation the cross-sectional SE yield coming from a CNT can be modelled by using the dimensions of a CNT. An example of two such SE yields is shown in Fig. 3.5 (a) obtained using two different values of \( \alpha \). As there are no experimental values of \( \alpha \) for CNTs listed in the literature, we used the absorption coefficient for carbon...
3.2 Scanning electron microscopy

Figure 3.5: (a) Plots of the total SE yield, obtained using different values of $\alpha$, along with the CNT dimensions used as input. (b) Simulated height normalised intensity profiles obtained using the secondary electron yield in (a).

$\alpha = 1/20\text{nm}^{-1}$ listed in [70]. The SE yield is fairly insensitive to changes in $\alpha$, as is shown in Fig. 3.5 (b) where two $\delta$, obtained using different values of $\alpha$, are plotted. Having an infinitely sharp electron-probe shape, i.e $d_p = 0$, an integrated intensity profile of a CNT from an SEM image would look like Fig. 3.5 (a). But the size of the electron probe is finite and can be described by $i(r)$. The resulting SEM image will then be a convolution of $\delta_{\text{sim}}(r)$ with $i(r)$: 

$$I(r) = [\delta_{\text{sim}} * i](r) = \int \delta_{\text{sim}}(r')i(r - r')dr'$$  \hspace{1cm} (3.8)

When imaging details that are large compared to the electron-probe, the convolution would be negligible. For details comparable in size to the electron probe, $i(r)$ blurs the image significantly. This is illustrated in Fig. 3.5 (b), where $\delta_{\text{sim}}$ has been convoluted...
with a Gaussian electron-probe shape:

\[ i_G(r) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{r^2}{2\sigma^2}\right) \]  

(3.9)

and with a Lorentzian electron-probe shape:

\[ i_L(r) = \frac{1}{\pi \Gamma_L \left(r^2 + \left(\frac{1}{2}\Gamma_L\right)^2\right)} \]  

(3.10)

A full width at half maximum (Γ) of 2.1 nm was used for both electron-probe shapes. Where the Γ\(_G\) = 2\(\sqrt{2\ln2}\)\(\sigma\) and Γ\(_L\) is the full width at half maximum for the Gaussian and the Lorentzian distribution respectively. Comparing Fig. 3.5 (a) and (b) it is apparent that the resulting intensity distribution is much smoother than the SE yield.

The convolution in Eq. 3.8 was performed in MATLAB where the products of small elements of \(\delta_{\text{sim}}(r)\) and \(i(r)\) were added together numerically. The integrations limits were chosen to be \([R + 5\Gamma, R - 5\Gamma]\) since both \(i_G(r)\) and \(i_L(r)\) quickly go to zero.

### 3.2.2.1 Simulation

The model of how the SEM image is constructed (Eq. 3.7), was tested on SEM images of CNTs. Individual CNTs were first imaged in a JEOL (JEM 2100) TEM equipped with a LaB\(_6\) cathode and a digital camera from Gatan (SC1000 Orsius). The samples consisted of two types of MWCNTs obtained from Nanocyl: NC2100 and NC2101, described in more detail in section 4.2.1. The CNTs were first dispersed in ethanol and then sonicated for 15 min to reduce bundling, thus simplifying imaging of individual CNTs. The suspension was drop-casted onto holey carbon support films for TEM (R 2/1 produced by Quantifoil). In these samples, individual CNTs stuck out over the holes in the carbon film and could be imaged without any underlying substrate. The same individual CNTs were subsequently imaged in a LEO 1530 FEG-SEM using the in-lens detector. The films were mounted in a custom made scanning transmission electron microscopy holder for the SEM. This holder enabled imaging of the same CNTs without any underlying substrate. Before exposing the samples to the electron beam, they were left in the SEM chamber for at least 10 hours, giving an SEM-chamber pressure of about 5 \times 10^{-7} mbar. This was done in order to minimize electron beam-induced deposition (EBID), which can build up amorphous carbon on the CNTs and increase their diameters [71]. To further reduce EBID, the CNTs were only exposed to
the beam while imaging and the amount of EBID was later checked by subsequently examining the same CNTs in the TEM. Only negligible amounts of EBID were seen in our samples during the final TEM imaging. Another way of checking the amount of EBID is to look at SEM image sequences and see if the image changes with time, but this is much less accurate than using a TEM.

![Figure 3.6: TEM (a) and SEM (b) image of the same CNT. The boxes in (a) and (b) show the areas from where the integrated intensity profiles were obtained. Along with the integrated intensity profile form the SEM image simulated intensity profiles are plotted in (c), obtained using different i(r).](image)

From the TEM images the inner and outer diameters of the CNTs were obtained and used to get an expression for $\delta_{\text{sim}}$. Linear combinations of $i_G(r)$ and $i_L(r)$ (Eq. 3.9 and 3.10), having the same $\Gamma$, were used as $i_{\text{sim}}(r)$ in order to reproduce the integrated
3. EXPERIMENTAL

intensity profiles of the SEM image. On average it was found that an electron-probe shape consisting of:

\[ i_{\text{SEM}}(r) = 0.5i_G(r) + 0.5i_L(r) \]  \hspace{1cm} (3.11)

having \( \Gamma_G = \Gamma_L = 2.05 \pm 0.05 \text{ nm} \) reproduced our SEM images satisfactorily. An example of this is shown in Fig. 3.6.

\[ \text{Figure 3.7: Raw (a) and deconvoluted (b) SEM images. The integrated intensity profiles from the boxes in (a) and (b) are plotted in (c). The inner diameter is more clearly seen in the deconvoluted image.} \]

A two dimensional version of Eq. 3.11 was also used to deconvolute SEM images of CNTs, by using it as the input point-spread function in the MATLAB-function \texttt{deconvblind}. An image deconvoluted in this way is shown in Fig. 3.7 along with the raw SEM image and a comparison of their intensity profiles. It is apparent from Fig. 3.7 that the image gets sharper and reveals more detail than the raw image, but the deconvoluted intensity profile is still far from the SE yield shown in Fig. 3.5. One
3.2 Scanning electron microscopy

reason for this discrepancy is that there is random noise in the raw SEM image. This noise is not related to the electron-probe shape and hence cannot be further resolved by the deconvolution. In order for a deconvolution to work well, \( i(r) \) has to be accurately described. A method for determining the size of \( i(r) \) have been suggested \cite{72}. However this method assumes a completely Gaussian shaped \( i(r) \) and cannot determine probe sizes smaller than 2 nm.

Using the model described above to simulate intensity profiles renders a good estimation of \( i(r) \) but requires prior knowledge about the CNT dimensions, in our case obtained from TEM images. Using the image formation mechanisms we developed a method where accurate estimations of the outer CNT diameter can be made without requiring a detailed description of \( i(r) \). This method uses the distance between the points where the intensity profile’s second derivative changes sign (zero points) as the diameter of the CNT, as illustrated in Fig. 3.8.

![Figure 3.8](image_url)

**Figure 3.8:** The TEM and SEM profiles from Fig. 3.6 are shown along with a polynomial fit to the SEM profile and its second derivative.

Looking at a convolution of a step function, \( H(r-r_0) \), and an arbitrary symmetric electron-probe shape \( I_H(r) = [H * i](r) \), its second derivative changes sign when the maxima of \( i(r) \) meets the edge. However, the SE yield of a CNT is not a step function, but it does have sharp steps at the start and end. Taking the derivative of an intensity profile directly is not possible because of the noise in the image. We therefore fitted a 10th order polynomial to the intensity profile, yielding a smooth enough function to differentiate. It is important that the polynomial fit follows the experimental data and the SEM image should therefore have a high signal-to-noise ratio. We have used the
zero points of the polynomial fit to $\frac{d}{dr}I(r)$ to estimate the CNT diameter from SEM images, $d_{SEM}$, for a number CNTs. These estimations were compared to the diameters measured in TEM images, $d_{TEM}$. Good agreement between $d_{SEM}$ and $d_{TEM}$ was obtained as is shown in Fig. 3.9 (a).

![Figure 3.9](image)

**Figure 3.9:** (a) Diameters from the second derivate method versus the diameter obtained from TEM images. Gray line shows the estimated diameter from simulations (using $\Gamma = 1 - 3$ nm). (b) Estimated diameters versus true diameter for different probe sizes.

The accuracy of this method was studied by simulating various intensity profiles, using Eq. 3.11 as $i(r)$ with $\Gamma = 1 - 3$ nm. The CNT used to obtain $\delta_{sim}$ had an inner diameter of 1 nm and additional layers where added to get a thicker CNT. The results of these simulations are shown in Fig. 3.9 (b), and one can see that the method estimates the outer diameter accurately for $\Gamma < d_{outer}$. When $\Gamma$ is larger than the outer diameter the method overestimates the outer diameter, but for $d_{outer} > \Gamma$ it is independent of $\Gamma$. 
3.3 Transmission electron microscopy

In a TEM, the purpose of the electromagnetic lenses before the specimen is to form a broad parallel beam that illuminates the area of interest. The beam path is therefore different to the path in a SEM where a focused probe hits the specimen. The beam cannot be made completely parallel. So the beam will always have a slight convergence angle hitting the specimen, impairing the final resolution. This angle can be controlled by adjusting the lenses or by using apertures of different diameters. However, this affects the intensity of the beam where the intensity is being reduced when the convergence angle is reduced. So there is a trade-off between having a large intensity and a small convergence angle.

A simplified beam path after a parallel beam has hit the specimen is shown in Fig. 3.10. After hitting the specimen some electrons will travel straight through the specimen whereas some electrons will be scattered, either diffusively or coherently. First in the column comes an objective lens aiming at creating an image of the specimen. After this lens an image plane and a focal plane can be found. An image plane is where rays originating from the same point in the specimen again come together in one point, and a focal plane is where rays scattered at the same angle meet in one point. An aperture can be inserted to an image plane to select an area of interest. This is used when performing selected area diffraction, i.e. diffraction coming only from an area of interest. An aperture can also be inserted in a focal plane to remove electrons diffracted at large angles, giving a diffraction contrast in the final image. A smaller aperture can be used in the focal plane to only let electrons diffracted at a certain angle continue down the column. These electrons will then form a dark field image. Further down the column the intermediate lens is found. This lens controls whether a magnified image or a diffraction pattern is projected on the fluorescent screen. Finally the projector lens focuses the beam onto the fluorescent screen.

All electrons scattered, diffusively or coherently, hold information about the specimen and will give contrast to the final image or diffraction pattern. Diffuse scattering comes from unsorted objects in the specimen. The contrast coming from such objects are a mass-thickness contrast since heavier nuclei have a larger scattering cross-section and thicker sections scatter more.
Figure 3.10: Ray diagrams in a TEM after the specimen (a) image mode (b) diffraction mode.

An amorphous specimen, e.g. a supporting carbon film, can be used to adjust the astigmatism of the objective lens. This is done by applying a fast Fourier transform (FFT) to a live image. Since the specimen is amorphous the electrons will be diffusively scattered in all direction and the FFT should therefore be in a shape of a disc. If this disc is elliptical the stigmators needs to be adjusted until an circular disc is obtained.
3.3 Transmission electron microscopy

3.3.1 Phase-contrast in TEM

An important contrast mechanism in crystalline specimens is the phase contrast, which arises when two or more beams in the diffraction space form an image. The normal case is that the direct beam (having \( \vec{k} = \vec{k}_0 \)) interacts with one or more diffracted beams (having \( \vec{k} = \vec{k}_D \)). The difference between the wave vectors is then the reciprocal lattice vector of the specimen, \( \vec{G} \):

\[
\Delta \vec{k} = \vec{k}_D - \vec{k}_0 = \vec{G}
\]  

The wave equation for the two beams can then be written as:

\[
\psi = A_0 e^{-2\pi i \vec{k}_0 \cdot \vec{r}} + A_D e^{-2\pi i \vec{k}_D \cdot \vec{r}}
\]  

where \( A_0 \) and \( A_D \) are the amplitude of the direct beam and the diffracted beam respectively. Eq. 3.13 can be rewritten using the relation in Eq. 3.12 as:

\[
\psi = e^{-2\pi i \vec{k}_0 \cdot \vec{r}} \left( A_0 + A_D e^{2\pi i \vec{G} \cdot \vec{r}} \right)
\]

The intensity, \( I \), detected by the fluorescent screen or camera is described by:

\[
I = \psi \psi^* = A_0^2 + A_D^2 + A_0 A_D \left( e^{-2\pi i \vec{G} \cdot \vec{r}} + e^{2\pi i \vec{G} \cdot \vec{r}} \right)
\]

Eq. 3.15 can be rewritten as:

\[
I = A_0^2 + A_D^2 + 2 A_0 A_D \cos(2\pi \vec{G} \cdot \vec{r})
\]

From Eq. 3.16 it is seen that \( I \) varies periodically with respect to \( \vec{r} \) having the reciprocal lattice vector as the period. This is a very simple picture since no care has been taken to the specimen except its reciprocal lattice. The thickness of the sample also affects the phase and the amplitude of the diffracted beam. This can be accounted for by replacing the amplitude \( A_D \) with \( \xi \) :

\[
A_D = \frac{\pi}{\xi_g} \frac{\sin(\pi t s_{eff})}{\pi t s_{eff}} e^{i\left(\frac{\pi}{2}\right)t s_{eff}}
\]

where \( \xi_g \) is the extinction distance, \( t \) is the thickness, and \( s_{eff} \) is the effective excitation error.

The phase contrast enables atomic planes to be viewed with high resolution TEM, since they have a resolution of about 0.2 nm. In Fig. 3.11 (a) a TEM-image is shown,
3. EXPERIMENTAL

where the individual walls of a MWCNT and also an intralayer plane in graphite with a spacing of 0.21 nm is resolved. In Fig. 3.11 (b) a FFT of the image in (a) is shown. Highly crystalline MWCNTs yields a FFT of very sharp spots and it has been suggested that the FFT could be used to quantify the crystallinity of MWCNTs [73].

The resolution of TEM is limited by the spherical aberration which is an inherent property of magnetic lenses, see section 3.1.2. TEMs having correctors for the spherical aberration have been able to resolve individual atoms [74, 75].

![Figure 3.11: (a) TEM-image of a MWCNT. (b) FFT of the image in (a).](image)

3.3.2 Beam-specimen interaction

When the beam hit the specimen some of the electrons will transfer energy to the atoms of the sample. This energy transfer can break bonds or even knock atoms out of the sample. If a bond is broken this will leave dangling bond in the specimen which is highly reactive and will thus easily react with the external nearby atoms. External nearby atoms could be amorphous carbon deposits or atoms in the atmosphere. If no external atoms are in the immediate vicinity the created dangling bond will return to the original bonding configuration. If an atom is knocked out, one atom will be missing from the specimen lattice and there will be several dangling bonds from the neighbouring atoms that will easily react with external nearby atoms. If there are reactions with external atoms more atoms can be ejected. However there can also be a bond recombination in the specimen connecting all the dangling bonds and forming a stable defect.

The threshold for knock-on damage in graphene has been found to be about 80 kV, [75] i.e. using larger acceleration voltages will knock atoms out of graphene. At 80 kV
and below the bonds in graphene can still be broken making the atoms in the graphene lattice more susceptible to react with external atoms. Since CNTs have a similar lattice to graphene the same should be valid for them. It has been shown that an acceleration voltage of 80 kV can structurally modify CNTs, in the presence of amorphous carbon or defects [76]. In the same reference they also showed that small diameter CNTs are more susceptible to electron beam modification due to the higher strain and misalignment of the π-orbitals. Therefore care must be taken when imaging and measuring properties of carbon nanostructures are made in TEM. Before measuring CNT properties the CNT

Figure 3.12: (a) TEM-image of a CNT with surrounding fullerenes just after being exposed to an electron beam with $V_{\text{acc}} = 80$ kV. The regions i-iii highlight regions of amorphous carbon. (b) The CNT is pushed against a force sensor that is covered with amorphous carbon that region iv comes in contact with. The CNT buckles in region iii. (c) After the CNT and the surrounding fullerenes have been exposed to the electron beam.
3. EXPERIMENTAL

should be exposed to the electron beam as short time as possible and with an intensity as low as possible. A larger acceleration voltage than 80 kV will cause knock-on damage in CNTs which will create a lot of defects that severely can impair the properties of the CNT. But also an acceleration voltage lower than 80 kV can modify the structure if amorphous carbon or other external atoms are in contact with the irradiated CNT.

Fig. 3.12 serves as an example of what can happen if a CNT is exposed to a high electron intensity in the vicinity of amorphous carbon. All images in Fig. 3.12 were acquired using an acceleration voltage of 80 kV, i.e. below the threshold for knock-on damage for graphene/CNTs. Fig. 3.12 (a) show a CNT when it just has been exposed to the electron beam. The boxes i-iii in (a) highlight areas where amorphous carbon are present. In Fig. 3.12 (b) the free end of the CNTs comes in contact with the force sensor causing the CNT to bend. The region of the force sensor that is in contact with CNT is covered with amorphous carbon which is why box iv is highlighted. The CNT buckles in the region of box iii, so the local strain in this region is greater than in other regions along the CNT. Fig. 3.12 (c) shows the CNT after it has been exposed to the electron beam for a considerably long time. It can be seen that in all the highlighted regions the walls of the CNT have been damaged. It is most apparent in region iii where the local strain is high and the CNT is in contact with amorphous carbon.
3.4 In situ SEM/TEM-AFM

Measurements of the stiffness of individual CNTs were made using a custom built in situ SEM-AFM and a Nanofactory Instruments in situ TEM-AFM [8]. Both instruments were controlled by software and electronics from Nanofactory Instruments. The instruments are schematically identical and comprise of a tip holder attached to a piezoelectric tube and an opposing force sensor, as shown in Fig. 3.13. The sample is attached at the end of a metal tip which is fastened to the tip holder. This has six metal springs embracing a sapphire ball that is attached to the piezoelectric tube. By applying sawtooth voltages to the piezoelectric tube, the tip holder will slip against the sapphire ball and can thereby be moved in all three dimensions. This inertial slider mechanism provides coarse motion of the sample in three dimensions and is described in more detail in [77]. The force sensor is a piezoresistive AFM cantilever that was micromachined on an n-type silicon on insulator chip [8]. On one face of the cantilever, a shallow ion-implantation of boron was made, creating a piezoresistor that changes resistance when the material is strained. Thus a deflection of the cantilever alters the resistance of the piezoresistor. By including this piezoresistor in a Wheatstone bridge, consisting of another identical dummy piezoresistor and two known resistances, the output bridge-voltage will be proportional to the force exerted on the cantilever.

![Figure 3.13: Schematic drawing of the in situ SEM/TEM-AFM instrument.](image)

3.4.1 Calibration of the in situ instruments

Calibration of the in situ SEM/TEM-AFM instruments requires calibration of the piezoelectric tube movement and the AFM sensor. The motion of the piezoelectric tube was calibrated by applying a voltage to it and measuring the resulting displacement inside the SEM and TEM, giving a constant, \( \frac{dz}{dU} \). The displacements were obtained by measuring the change in distance between the tip and a static reference surface, as
3. EXPERIMENTAL

shown in Fig. 3.14 (a)-(c). This was done in small voltage steps, both going forward and backward, in order to account for the piezoelectric creep. Obtained displacements were plotted against the applied voltages and a linear function was fitted to the plotted values, as shown in Fig. 3.14 (d). This was done for a number of runs and the mean value of the obtained slopes was used as the constant $dz/dU$ in the software controlling the piezoelectric tube.

![Figure 3.14](image-url)

Figure 3.14: (a)-(c) SEM-images of a static reference surface (top) and the movable tip (bottom). Voltages were applied to the piezoelectric tube, causing a movement of the tip towards the static reference surface. The change in distance between the tip and the reference surface was used to obtain the displacement of the piezoelectric tube at the applied voltage. (d) A plot of the displacements, $z$, versus the applied voltages, $U$, yields the constant $dz/dU$.

Calibration of the AFM sensor requires a calibration of two constants: the piezoresistive constant $C$ [mV/nm] of the piezoresistor, and the spring constant $k$ [N/m] of the cantilever. This was done by gluing a reference cantilever to a wire, and mounting this wire in the tip holder. The reference cantilevers (NSC18/F/AIBS/5) were obtained from MikroMasch, and had been calibrated using the plan view dimensions and the resonant frequency of the cantilever in a fluid [78]. By pushing a part of the rigid silicon
wafer against the piezoresistive cantilever the piezoresistive constant was calibrated, as shown in Fig. 3.15 (a). This was done by applying a voltage to the piezoelectric tube, displacing the reference cantilever a distance $\Delta z$. The wafer, consisting of Si, was assumed to be rigid. Hence the piezoresistive cantilever was also displaced $\Delta z$, generating a voltage signal, $\Delta U$. This $\Delta U$ was plotted versus $\Delta z$ and the mean value of slopes in such graphs were taken as the constant $C$.

Figure 3.15: SEM images taken during (a) calibration of the piezoresistive constant and (b) the spring constant of the sensor cantilever. The calibration was done by pushing a rigid surface in (a) and a reference cantilever in (b) against the sensor cantilever (to the left).

The spring constant of the piezoresistive cantilever was calibrated by pushing the reference cantilever against it, as shown in Fig. 3.15 (b). By applying a displacement $\Delta z_{\text{applied}}$ to the piezoelectric tube, both the reference cantilever and the sensor cantilever will be deflected through: $\Delta z_{\text{applied}} = \Delta z_{\text{sensor}} + \Delta z_{\text{reference}}$. The displacement of the sensor was obtained from the voltage output using the piezoresistive constant $C$ calibrated in the previous step. Using the relation between the displacements one can derive the relation between the spring constants of the sensor and the reference cantilever:

$$k_{\text{sensor}} = k_{\text{reference}} \left( \frac{\Delta z_{\text{applied}}}{\Delta z_{\text{sensor}}} - 1 \right)$$

(3.18)

The ratio $\frac{\Delta z_{\text{applied}}}{\Delta z_{\text{sensor}}}$ was obtained from the slopes in graphs where $\Delta z_{\text{sensor}}$ was plotted versus $\Delta z_{\text{applied}}$. As the spring constant of the cantilever is highly dependent on its length, or where the force is applied, the reference cantilever was pushed against the outermost part of the sensor, i.e. the same part used in subsequent force measurements.
3. EXPERIMENTAL

3.4.2 Force measurements

Soot particles containing CNTs were attached to a silver tip using electrically conductive epoxy, the sample preparation is more thoroughly described in section 4.2.1. This tip was then mounted in the in situ AFM instrument described in section 3.4, enabling 3D motion of the sample. To be able to locate suitable CNTs and measure their dimensions, the in situ AFM instrument was mounted inside an SEM/TEM. Straight tubes with no visible defects or amorphous carbon on them and attached so that they were parallel to the AFM cantilever, were located and brought in contact with the AFM cantilever. This setup is analogous to the cantilever-to-cantilever setup used when calibrating the AFM cantilever, described in section 3.4.1, with the difference that the CNTs are significantly smaller than the AFM cantilever. Overview images of the setup inside the SEM are shown in Fig. 3.16.

![Figure 3.16: (a)-(e) SEM-images of the experimental set-up at different magnifications.](image)

In (a) the AFM cantilever and the soot particle are clearly visible. (b) A magnification of the AFM tip. (c) A CNT close to the AFM cantilever. In (d) and (e) the CNT shown in (c) is pushed against the AFM cantilever.

From the SEM images, the diameter, \(d\), and the length, \(l\), of the CNT can be obtained. The length was estimated by measuring the displacement of the CNT as a function of the distance from the point of the applied force, \(\delta(x)\), see Fig. 3.17. Using the method of least squares with \(l\) as the fitting parameter, the function of a bent cantilevered beam was fitted to the measured displacements. From beam theory the
3.4 In situ SEM/TEM-AFM

Displacement of a cantilevered beam subjected to a point force at the free end is given by:

$$\delta \left( \frac{x}{l} \right) = \frac{\delta_0}{2} \left( \left( \frac{x}{l} \right)^3 - 3 \left( \frac{x}{l} \right) + 2 \right)$$

(3.19)

where $\delta_0$ is the displacement at $x = 0$.

**Figure 3.17:** A schematic showing how the length of the CNTs was determined. Vertical distances was measured from a line drawn from a fixed point on the sample for an unloaded (top) and for a bent CNT (bottom). The difference between these distances gives the deflection of the CNT as a function of $x$, $\delta(x)$.

It was found, by comparing TEM- and SEM-images of the same CNT, that the diameter could be estimated by taking the FWHM of a Gaussian function fitted to the SEM intensity profile. This was examined more thoroughly, and it was found that a more accurate method is to fit a high order polynomial to the intensity profile and finding the second derivative zero points of this fit. The distance between these points gives the diameter of the CNT. This method is described in section 3.2.2 and in Paper II.

Pushing the CNTs against the cantilever gives $F$-$\delta$ curves, where the force detected by the cantilever is plotted versus the piezo-displacement. An example of a $F$-$\delta$ curve is seen in Fig. 3.18.

As can be seen in Fig. 3.18 the spring constant abruptly changes at a certain critical displacement $\delta_{\text{piezo}}^{\text{cr}}$. The critical displacement of the CNT, $\delta_{\text{CNT}}^{\text{cr}}$, is related to the critical displacement of the piezo through:

$$\delta_{\text{CNT}}^{\text{cr}} = \delta_{\text{piezo}}^{\text{cr}} \left( 1 - \frac{k_{\text{piezo}}}{k_{\text{cant}}} \right)$$

(3.20)

where $k_{\text{piezo}}$ and $k_{\text{cant}}$ is the spring constant obtained from the $F$-$\delta$ and the spring constant of the cantilever respectively. Using $\delta_{\text{CNT}}^{\text{cr}}$ and assuming the CNT to be
3. EXPERIMENTAL

Figure 3.18: $F$-$\delta$ curve obtained by pushing an cantilevered individual CNT. Black dots are from forward motion and hollow dots are from moving backwards. At a critical displacement the spring constant of the CNT drastically changes. This change is reversible since the force response is identical when moving backwards.

equivalent to a cantilevered beam with circular cross-section, the maximum critical strain can be calculated using:

$$\varepsilon_{cr} = \frac{3\delta_{CNT}}{l^2}$$  \hspace{1cm} (3.21)

where \(r\) and \(l\) is the radius and length of the CNT respectively.

Other useful parameters from the $F$-$\delta$ curve are the spring constants $k_{tot}^i$ and $k_{tot}^r$. These are related to the spring constant of the CNTs, $k_{CNT}$, through:

$$k_{CNT} = \frac{k_{tot}^i k_{tot}^r}{k_{tot}^i + k_{tot}^r}$$  \hspace{1cm} (3.22)

where $k_{cant}$ is the spring constant of the cantilever. Using $k_{CNT}^i$ and assuming the CNTs to be equivalent to cantilevered beam with a circular cross-section with inner and outer radius $r_i$ and $r_o$ respectively, the Young’s modulus can be calculated using:

$$E = \frac{4k_{CNT}^i l^3}{3\pi r_o^4} \times \frac{r_o^4 - r_i^4}{r_o^4 - r_i^4}$$  \hspace{1cm} (3.23)

There is no way of measuring very small $r_i$ using SEM, but the factor $r_o^4/(r_o^4 - r_i^4)$ quickly goes to 1 as the ratio $r_i/r_o$ decreases. When studying the CVD-grown CNTs in a TEM it was found that most CNTs had $r_i/r_o \leq 0.5$ resulting in $r_o^4/(r_o^4 - r_i^4) \leq 1.07$, hence the factor $r_o^4/(r_o^4 - r_i^4)$ in Eq. 3.23 can be neglected.
Chapter 4

Materials

4.1 Synthesis methods

Literature on the synthesis of tubular carbon structures is abundant and there are several synthesis methods [3, 79], resulting in different structures. In this chapter, only a short description of the most common methods will be presented. These methods are arc discharge, laser ablation, and chemical vapor deposition.

4.1.1 Arc discharge

The MWCNT studied in the paper by Iijima [1] were obtained by putting two graphite electrodes in close proximity, about 1 mm, in a controlled argon atmosphere. Variations of this method have been used in a number of studies where the gas in the atmosphere can be altered as well as the pressure in the chamber. When a voltage is applied between the electrodes a plasma is first formed by the gas. The heat from this plasma vaporizes carbon atoms that become part of the plasma. Ionized carbon atoms are then attracted to the positive electrode where they condensate and form various sorts of carbon, including amorphous carbon, fullerenes, and of course CNTs. The final product thus needs purification steps in order to get a pure CNT sample. By using pure graphite electrodes, only MWNCTs are grown, but by including metal catalysts, e.g. Co, Ni, or Fe in the negative electrode, SWCNTs are grown [12, 13].

CNTs synthesized using this method are straight and needle-like, indicative of high crystalline quality, i.e. a small defect density. One drawback of this method is the small
4. MATERIALS

production yield of CNTs. Another problem is the high level of by-products that have to be removed, making this method unsuitable for large scale production.

4.1.2 Laser ablation

In the laser ablation method, like in the case of arc discharge, CNTs are formed from vaporized graphite. In this method a target, containing of graphite mixed with small amounts of catalytic metals, e.g. Ni, Co, or Fe, is exposed to intense laser pulses that vaporizes small amounts of the target per pulse [80]. The target is placed in a heated tube furnace, \( T > 1000^\circ\text{C} \), in which an inert gas is passed. CNTs are formed in the plasma created by the laser and carried from the target by the inert gas towards a cold finger on which they condensate.

CNTs obtained using this method are small in diameter with few walls of high crystalline quality. However the drawback of this method is, as in the case of arc discharge, that it cannot be scaled up to create large amounts of CNTs.

4.1.3 Chemical vapor deposition

Chemical vapor deposition (CVD) is different from the two previous methods since it is easily scaled up to produce large amounts of CNTs. In principal this method consists of a volatile gas, containing carbon, that is decomposed, enabling growth of CNTs from catalyst particles [79]. Growth takes place in a chamber, in which the volatile gas is fed along with other gases. The pressure and temperature of the chamber vary for different CVD methods. The catalyst particles can be patterned on a substrate before growth, created by decomposition of volatile gases, or simply fed as particles along with the gas in the chamber. This enables growth from substrate supported catalysts or from floating catalysts.

There are numerous models proposed to elucidate the growth process from a catalyst particle. Most models are based on the vapor-liquid-solid (VLS) mechanism [81] where carbon is absorbed by a liquid catalyst particle that eventually becomes supersaturated, leading to nucleation of carbon structures. However, no model can predict what happens at the catalyst and no CVD process can yet exactly control the chirality or the diameter of the resulting CNTs.

Because of the many variables involved in CVD methods, the resulting structures from different CVD methods vary a lot and can be tailored to yield predominantly
SWCNTs, MWCNTs or vertically aligned carbon nanofibers (VACNFs). In general the resulting structures are of lower crystalline quality than CNTs obtained from arc discharge and laser ablation. This lower crystalline quality can be seen in TEM-images where CVD-grown tubes are less straight and less needle-like. The walls also have small perturbations that are seldom present in highly crystalline CNTs. The advantage of this method is the feasibility of large scale production, and there are now a number of companies producing large quantities of CVD-grown CNTs.

4.2 Materials used

In this thesis three types of materials were used: commercial CVD-grown MWCNTs, MWCNTs grown by arc-discharge, and CVD-grown VACNFs. A description of these materials is found below.

4.2.1 Carbon nanotubes

In this work CNTs grown by two synthesis methods were studied: arc-discharge and CVD. Two types of CVD-grown CNTs were obtained from Nanocyl: NC2100 and NC2101 [82]. Both types were synthesized using a method Nanocyl calls “catalytic carbon vapor deposition”. The difference between the two types is that NC2101 had been functionalized with a carboxylic acid group (-COOH) in order to reduce bundling. The amount of -COOH in the samples is however very low, less than 1% [82], so it should not affect the material properties much. Further on in this thesis, the NC2100 and NC2101 types will be referred to as CNT and f-CNT respectively, where f highlights the functionalization.

The powder resulting from the synthesis is purified by Nanocyl, aiming at removing catalyst residues and amorphous carbon. After the purification, the powder is said to contain more than 90% carbon and less than 10% catalyst residues. Nanocyl also states, after imaging in TEM and SEM, that the CNTs are preferentially double-walled and that their average outer diameter and length are 3.5 nm and 1-10 \( \mu \)m respectively. Although the mean values for the diameter is relatively small, our samples contained CNTs with diameter larger than 18 nm, when studied in TEM and SEM. The large diameter CNTs often had small inner diameters.
4. MATERIALS

MWCNTs grown by the arc-discharge method were obtained from Professor Hui-Ming Cheng at the Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China. The material were received as carbon soot containing highly crystalline MWCNT along with other highly crystalline carbon species, e.g. nano-onions and other fullerenes. The synthesis was carried out without using any metal catalysts, so no residual metal particles were left in the received carbon soot. The range of diameters of the MWCNTs were large, but typically they were larger than in the case of the CVD-grown tubes.

Figure 4.1: TEM-images of the two types of MWCNTs used in this study, where the tubes were grown by (a) arc-discharge and (b) CVD.
In Fig. 4.1, TEM-images of the MWCNTs grown by arc-discharge and CVD are shown. From these images it is clear that the tubes grown by arc-discharge possess a higher crystallinity than the CVD-grown tubes. All tubes grown by arc-discharge are straight and needle-like whereas some of the CVD-grown tubes are curled up while others are straight. Looking at a larger magnifications, the walls of the tubes grown by arc-discharge is straighter compared to the straightest CVD-grown tubes, where the walls have a waviness. So far there is no method to evaluate the crystallinity quantitatively, but there have been suggestions to use a fast Fourier transform (FFT) of a segment of the tubes. A high crystallinity would result in a FFT consisting of sharp narrow spots [73]. However, this method would be dependent on the performance of the TEM and thereby difficult to use as an absolute measure.

Samples used in the in situ instrument (described in section 3.4) are attached to a thin metallic wire, thereby requiring some sample preparation. The CNT containing powder was dispersed in a solvent, where ethanol was used for the CVD-grown tubes while dichloroethane was used for the tubes grown by arc-discharge. Dichloroethane is a popular solvent for MWCNTs, [83] but chlorinated solvents can, in the presence of Fe nanoparticles, cause doping and disrupt the electronic band structure of CNTs [84]. In the case of the tubes grown by arc-discharge no metal particles were present, thus no doping could occur. However the CVD soot contained catalyst metal residues which could cause doping, which is why ethanol was used in this case.

The dispersions were sonicated for about 15 min in order to separate the tubes so that individual ones could be probed. Sonication for longer times could cause mechanical damage to the CNTs [85]. CNTs were therefore studied in TEM, showing no signs of mechanical damage after treatment. Droplets of the CNT-ethanol suspension were placed on a clean glass substrate and allowed to dry, resulting in well separated soot particles with a diameter of about 100 µm. Individual particles were then attached to thin silver wires by first coating the wire tip with conducting epoxy and then picking up particles under an optical microscope, see Fig. 3.13 for experimental set-up.

**4.2.2 Vertically aligned carbon nanofibers**

The growth of the VACNFs was made by a group from Chalmers University of Technology [59]. They used two different settings growing the VACNFs, resulting in two different structures: group A and B. Both settings started with deposition of 12 nm
thick Ni catalyst seeds on reactively sputtered TiN film on top of an oxidized silicon chip. The deposition was made using electron-beam lithography. This was followed by 1 hour annealing at 580°C in nitrogen at 6 mbar inside a AIXTRON 2-inch Black Magic reactor, in which the growth later was started. Both groups of VACNFs was grown using a dc plasma, with a power of 40 W, where the electric field, directed perpendicular to the substrate, aligned the fibers vertically from the substrate. Both groups were grown at substrate temperature of 635°C. For group A a chamber pressure of 3.5 mbar and a C$_2$H$_2$/NH$_3$ ratio of 1/4 was used, while a chamber pressure of 8.9 mbar and a C$_2$H$_2$/NH$_3$ ratio of 1/6 was used for group B. The relative amount of carbon-bearing species (e.g C neutrals and C ions) and etchant species (e.g H$^+$ and N$^+$) generated by the plasma is proportional and inversely proportional to the C$_2$H$_2$/NH$_3$ ratio respectively. Increasing this ratio will therefore increase the non-catalytic precipitation of carbon on the sample, leading to a larger deposition rate of amorphous carbon on the nanofiber during growth [59, 86]. This results in a tapered structure, where a thicker layer of amorphous carbon is deposited at the base of the fiber. Because of this, we define a taperedness factor:

$$\alpha = \frac{r_b - r_t}{l}$$

(4.1)

where $r_b$ and $r_t$ is the radius at the base and tip respectively and $l$ is the length of the fiber. More details about the growth of these VACNFs can be found in [58, 59].

Previous studies of similar VACNFs found that the core consist of a graphitic cup-stacked structure, shown in Fig. 4.2, where the graphitic planes have an angle $\theta$ to the fiber axis [86]. The graphitic planes follow the shape of the catalyst particle. Because of the catalyst particle geometry the graphitic planes are less closely packed in the center of the graphitic core, making this part appear hollow-like in TEM-images. A schematic sketch of the VACNF structure along with a TEM-image of a VACNF is shown in Fig. 4.2. From TEM studies we found that $\theta$ ranged from about 10° to 30°, and that the graphene cups mimic the shape of the catalyst particle.

In order to perform mechanical measurements on VACNFs, using the in situ SEM-AFM instrument, substrates were glued onto a silver wire using electrical conducting epoxy. In the synthesis process, substrates with the dimensions 11×2 mm were used. Using such large substrates makes the tip holder slip against the sapphire ball when moving the sample, due to gravitational forces. Predefined scratches were therefore made on the substrate prior to the synthesis. This facilitated cracking of the substrate.
4.2 Materials used

![Diagram of VACNF structure](image)

Figure 4.2: (a) Schematic sketch of the VACNF structure. (b) TEM-image of the top a VACNF. This VACNF was synthesized using a low C$_2$H$_2$/NH$_3$ ratio, yielding a very small taperness factor.

so that a smaller piece of the substrate, 3×2 mm, could be obtained and glued onto a silver wire. The substrate was positioned so that the VACNFs were parallel to the AFM sensor, facing the sensor in a cantilever-to-cantilever fashion.
4. MATERIALS
Chapter 5

Results and Discussion

5.1 Multi-walled carbon nanotubes

The mechanical behaviour of MWCNTs was studied by performing force measurements inside TEM and SEM. A typical measurement is shown in Fig. 5.1 where a cantilevered MWCNT is shown before being bent (a) and during bending (b). The resulting $F$-$\delta$ curve is shown in (c). When the MWCNT first comes in contact with the force sensor, at point 1 in (c), it behaves as a linearly elastic beam, i.e. the $F$-$\delta$ curve is linear. The slope of the force curve can be used to calculate the Young’s modulus using Eq. 3.23.

Results from this linear region is discussed in section 5.1.1. At point 2 in Fig. 5.1 (c) the MWCNT ripples, this is an important parameter for a number of applications and the rippling onset is discussed in section 5.1.2. After point 2 in Fig. 5.1 (c) the $F$-$\delta$ curve continues to be approximately linear albeit with a smaller slope. The behaviour of the MWCNT after the rippling onset is discussed in section 5.1.3.

5.1.1 Young’s modulus

The Young’s moduli of the tested MWCNTs are plotted versus their outer diameter in Fig. 5.2, where the CVD-grown are shown in (a) and the tubes grown by arc-discharge are shown in (b). Neither of the two plots show any clear dependence on the outer diameter. Early reports suggested that Young’s modulus decreased with increasing outer diameter[4]. In these studies $E$ was determined from resonance measurement, and the diameter dependence was proposed to originate from rippling deformations [4, 40, 87]. Tubes with a larger $d_o$ would ripple at smaller deflections and would
5. RESULTS AND DISCUSSION

Figure 5.1: (a) TEM-image of a MWCNT before being bent. (b) TEM-image of a MWCNT being bent well past the rippling onset. (c) Typical force-displacement curve showing a linear slope $k_1$, after the MWCNT comes in contact with the force sensor at point 1. At point 2 the MWCNT ripples and there is a sudden drop in stiffness. After this rippling onset the $F\delta$ relation is still approximately linear with spring constant $k_2$. The $F\delta$ curve follows the same route upon retraction.

Therefore appear to be softer. However, if only using the initial slope, prior to the rippling onset, no such $d_\omega$-dependence should exist, as our data in Fig. 5.2 shows.

Figure 5.2: Young’s modulus, $E$, plotted versus the outer diameter, $d_\omega$, for (a) CVD-grown MWCNTs and (b) MWCNTs grown by arc-discharge.

For a better comparison we can also plot the two data sets in a histogram, see Fig. 5.3. From this histogram it is apparent that the CVD-grown tubes possess a much smaller $E$ compared to the tubes grown by arc-discharge. Comparing their mean values,
5.1 Multi-walled carbon nanotubes

$E_{\text{CVD}} = 80$ GPa and $E_{\text{arc}} = 780$ GPa, the tubes grown by arc-discharge have an $E$ that is one order of magnitude higher. The reason for the big deviation is that CVD-grown tubes inherently contains more defects stemming from the synthesis. This fact has been known for several years, [35] but is often neglected in studies involving CNTs. It is often assumed that CNTs have extraordinary mechanical properties with $E = 1$ TPa without any clarification that only defect-free tubes possess this high Young’s modulus.

![Figure 5.3: Young’s modulus for two different growth techniques.](image)

5.1.2 Rippling onset

As described in the introduction of this chapter the critical strain for the rippling onset is an important parameter that can be extracted from the $F$-$\delta$ curve, using Eq. 3.21. In Fig. 5.4 the critical strain for CNTs grown by CVD and arc-discharge are plotted versus their outer diameter, along with three curves obtained from simulations [40, 41, 42]. Comparing the two growth processes, the CVD-grown tubes have significantly larger $\varepsilon_{\text{cr}}$ for similar diameter. Tubes grown by arc-discharge have a negligible defect density and thereby the inter-wall interaction is constituted solely of van der Waals forces. CVD-grown tubes on the other hand have a large defect density which can introduce covalent bonds between the layers [43]. This increases the inter-wall interaction resulting in a stabilizing effect against rippling of the outer walls from the inner walls. Therefore a larger defect density should increase the critical strain for the onset of rippling thus...
5. RESULTS AND DISCUSSION

Figure 5.4: The critical strain, $\varepsilon_{cr}$, plotted versus the outer diameter, $d_o$. The cited studies are Arias [41], Nikiforov [42], and Liu [40].

explaining the larger $\varepsilon_{cr}$ for the CVD-grown tubes. Simulations have indeed shown that a larger defect density shifts $\varepsilon_{cr}$ to larger values [88].

In the previous section we found that the defects in the CVD-grown tubes also lowered their Young’s modulus. So there could be a correlation between the Young’s modulus and the critical strain, i.e. a larger defect density would raise $\varepsilon_{cr}$ while lowering $E$. A plot of $E$ versus $\varepsilon_{cr}$ from our measurements, Fig. 5.5, show that a large $E$ is accompanied by a small $\varepsilon_{cr}$.

Figure 5.5: The Young’s modulus, $E$, plotted versus the critical strain, $\varepsilon_{cr}$.
5.1 Multi-walled carbon nanotubes

Though the tubes grown by arc-discharge should contain little defects, there are still some variations in the values for the critical strain, as can be seen in Fig. 5.4. Simulations [31, 41, 42] have found that the critical strain should depend on the outer radius as:

\[
\varepsilon_{cr} = \frac{l_{cr}}{r_o}
\]  

(5.1)

where \(l_{cr}\) is a constant, coined the critical length [41] since it has the dimension of a length. The modelled values of this constant varies from \(l_{cr} = 0.0385\) nm for SWCNTs, [31] to \(l_{cr} = 0.10\) nm for thick MWCNTs [41]. So there seem to be a dependence on the thickness of the MWCNTs, where thin tubes have a lower \(l_{cr}\) and vice versa.

To examine this further we plot our obtained values of the critical strain versus a normalized thickness, \(t_N = (d_o - d_i)/d_o\), in Fig. 5.6. From Fig. 5.6 it is apparent that \(l_{cr}\) increases with increasing \(t_N\).

![Figure 5.6: The critical length, \(l_{cr}\), plotted versus the normalized thickness, \(t_N\). The cited studies are Arias [41], Nikiforov [42], Yakobson [31], and Chang [89].](image)

Molecular mechanics simulations have found a slight increase of \(l_{cr}\) with increasing \(t_N\) [89]. The increase found from these simulations levelled of at a thickness of about \(t_N = 0.4\), as shown in Fig. 5.6. Our data show that the critical length increases even for large normalized thickness. We attribute the increase of \(l_{cr}\) to a supporting effect from the inner tubes and their radial stiffness that increases with \(t_N\). Treating the
5. RESULTS AND DISCUSSION

nanotube as a cylinder composed of a transversely isotropic material, having two in-plane Young’s moduli, $E_\varphi = E_z$, a radial Young’s modulus, $E_r$, and a Poisson’s ratio, $\nu_{r\varphi}$, the normalized radial stiffness can be written as:

$$S_N(t_N) = \frac{1 - (1 - t_N)^{2n}}{1 - \left( \frac{E_r}{E_\varphi} \right) (1 - t_N)^{2n}}$$  \hspace{1cm} (5.2)

where $n = \sqrt{\frac{E_\varphi}{E_r}}$. For a derivation of Eq. 5.2 see the supplemental information of Article IV. By assuming that $S_N$ increases the critical length from a minimum to a maximum value as $t_N$ varies, we used the following equation to fit the data in Fig. 5.6:

$$l_{cr}(t_N) = l_{cr}^{N=0} + (l_{cr}^{N=1} - l_{cr}^{N=0}) S_N(t_N)$$  \hspace{1cm} (5.3)

The resulting fit is plotted along with the data in Fig. 5.6 where the parameters giving the best fit were $l_{cr}^{N=0} = 0.038$ nm, $l_{cr}^{N=1} = 0.119$ nm, $\nu_{r\varphi} = 0.79$, and $n = 1.23$ (corresponding to $E_r = 520$ GPa by using $E_\varphi = 780$ GPa).

The value of $l_{cr}^{N=0}$ is valid for SWCNTs or thin-walled MWCNTs, i.e. $d_i \approx d_o$, and the best fit value agrees well with simulations on SWCNTs, where a value of $l_{cr} = 0.0385$ nm was obtained [31]. The value of $l_{cr}^{N=1}$ is valid for thick MWCNTs, i.e. $d_i \ll d_o$, and the best fit value agrees well with simulations on thick MWCNTs, where a value of $l_{cr} = 0.10$ nm was obtained [41]. The radial Young’s modulus may seem quite large, but similar values have been reported from measurements on MWCNTs [90]. Reported values of $E_r$, found through modelling and measurements, varies by almost three orders of magnitude [90, 91, 92, 93, 94, 95, 96, 97, 98, 99]. The Poisson’s ratio $\nu_{r\varphi} = \frac{\nu_{r\varphi}}{E_r}$ correspond to a contraction in the $\varphi$-direction when an extension is applied in the $r$-direction. The value obtained from the fitting satisfies the constraints on Poisson’s ratio for a transversely isotropic material ($\nu_{r\varphi}^2 < \frac{E_r}{E_\varphi}$) and similar values have been suggested from modelling [100].

We believe that the supporting effect, Eq. 5.3, also should be present in multiwalled nanotubes made from materials other than carbon, e.g. BN, WS$_2$, and MoS$_2$, although the values of $l_{cr}^{N=0}$ and $l_{cr}^{N=1}$ should be adjusted.

In summary, we have found that the rippling onset is dependent on the outer diameter, inner diameter, and the defect density. These factors need to be carefully considered when employing CNTs in configurations where they are bent and rippling is unwanted.
5.1 Multi-walled carbon nanotubes

5.1.3 Post-rippling behaviour

When bending carbon nanotubes they will have an abrupt drop in stiffness at the critical strain, as shown in Fig. 5.1 (c). After the rippling onset the $F-\delta$ curve continues to be linear, or near linear, albeit with a smaller spring constant. The ratio of the initial spring constant, $k_i$, and the spring constant of the rippled phase, $k_r$, is an important parameter for future NEMS applications. From the $F-\delta$ curve, the two spring constants can be extracted, using Eq. 3.22, and the ratio $k_r/k_i$, describing the retained bending stiffness, can be calculated.

![Graph](image)

Figure 5.7: The ratio $k_r/k_i$ plotted versus the Young’s modulus, $E$.

From our measurements we found that MWCNTs grown by arc-discharge had a larger drop in bending stiffness compared to CVD-grown tubes. So there seem to be a dependence between the defect density and the post-rippling stiffness. To investigate this further we plot the ratio $k_r/k_i$ versus the Young’s modulus, which can be seen as a measure of the defect density. In this plot, shown in Fig. 5.7, measured values from tubes grown by arc-discharge and CVD are included. The post-rippling stiffness is much higher for the CVD-grown tubes which retain about 40-70% of their initial stiffness after the rippling onset. This increase comes at a cost of a lower initial Young’s modulus, which were one order of magnitude smaller for the CVD-grown tubes compared to the tubes grown by arc-discharge, as discussed in section 5.1.1. There is a general trend for
5. RESULTS AND DISCUSSION

tubes with a high value of the ratio \(k_r/k_i\) also having a low value of \(E\). This indicates that defects increase the relative post-rippling stiffness, and also that not all MWCNTs grown by arc-discharge are defect free since some of them have a low value of \(E\) in combination with a high value of \(k_r/k_i\). Modelling have found that defects increase the post-rippling stiffness by increasing the inter-wall interaction [43]. The increased inter-wall interaction distributes the stress more evenly across the cross-section which counteracts the forming of kinks, hence both shifting \(\varepsilon_{cr}\) towards higher values and increasing \(k_r/k_i\). Even though our CVD-grown tubes had very low Young’s moduli, there could be certain defects that increase the inter-wall interaction without weakening the intra-wall bonds [43]. Such defects are yet to be confirmed experimentally though.

As discussed earlier the critical length, and thereby also the critical strain, is larger for tubes with a larger normalized thickness. To investigate whether there is also a dependence of the post-rippling stiffness on the normalized thickness, we plot \(k_r/k_i\) versus \(t_N\) in Fig. 5.8. However, given the influence of the defect density on the post-rippling stiffness, the large defect density of the CVD-grown tubes obscure an influence of \(t_N\) on \(k_r/k_i\). We therefore omit the CVD-grown tubes and only use values from the MWCNTs grown by arc-discharge. In the plot we have distinguished between tubes that developed a single kink and multiple kinks. Tubes that develop a single kink are referred to as buckled and are plotted with boxed black crosses, whereas tubes with multiple kinks are referred to as rippled and are plotted with black crosses.

The plot in Fig. 5.8 show that tubes with a small \(t_N\) preferably buckle, even though there is a range where both rippling and buckling occur. Above a normalized thickness of \(t_N > 0.8\), no tubes were observed to buckle. It should be mentioned that our definition of rippling and buckling is rather crude and in some cases it was hard to determine whether there were one or multiple kinks. The difficulty partly comes from our experimental set-up, where the bending moment increases linearly along the tube and reaches a maximum at the point of attachment. Hence, the strain is largest near the attachment point and in this region the rippling and buckling starts. Indeed, none of the tubes displayed a uniformly distributed rippling pattern. Instead the kinks were concentrated close to the point of attachment. This could explain why some tubes that seemed to only develop one kink retained up to 20% of their initial bending stiffness after the critical strain, when buckled tubes are expected to lose all their bending stiffness.
5.1 Multi-walled carbon nanotubes

![Figure 5.8: The ratio $k_r/k_i$ plotted versus the normalized thickness, $t_N$. The cited studies are Nikiforov [42], Chang [101], and Arroyo [7].](image)

At a first glance it seems as if $k_r/k_i$ increases with $t_N$, but the two data points with the highest value of the post-rippling stiffness belong to tubes with a low Young’s modulus (compare with Fig. 5.7). So the high values of $k_r/k_i$ for these tubes could stem from a larger defect density than the other tubes. Disregarding tubes with $E < 500$ GPa and the collapsed tubes with $k_r/k_i \approx 0$ the values of $k_r/k_i$ seem to be constant with respect to $t_N$ and have a mean value of 0.2. Modelling studies that investigated the behaviour of MWCNTs after the rippling onset have found varying results. One study showed a very strong dependence of the post-rippling stiffness on the normalized thickness, where $k_r/k_i$ increases rapidly with $t_N$ [42], whereas another study found a much weaker dependence [101]. The results from the two modelling studies are also plotted in Fig. 5.8. As our result show no dependence of $k_r/k_i$ on $t_N$ our measurements agree more with the study showing a weak dependence, though our values are lower than the modelled values. Another difference lies in the geometry, where both modelling studies have used a uniformly distributed bending moment as opposed to our linearly increasing moment. In Ref. 7 a cantilevered MWCNT was modelled and a value of about $k_r/k_i = 0.23$ was found, which is closer to our values.

In Fig. 5.9, a $F$-$\delta$ curve with a high signal-to-noise ratio is shown. Such low noise curves were only obtained for tubes with a large $k_i$, i.e. relatively short tubes with large $d_o$ and $t_N$. Three ‘critical points’ can be observed in the $F$-$\delta$ curve, shown in Fig.
5.9. At point 1 the MWCNT ripples and abruptly changes stiffness. The $F$-$\delta$ curve continues to be linear, albeit with a lower spring constant, up to point 2 where there is a sudden drop in the force. After this drop the force continues to increase linearly with respect to $\delta$. Upon retraction the $F$-$\delta$ curve follows this slope back until point 3 where there is a sudden increase in the force, although small.

![F-\delta curve](image)

Figure 5.9: $F$-$\delta$ curve with a high signal-to-noise ratio to the left and a graph highlighting the features of the $F$-$\delta$ curve to the left.

A similar behaviour, as shown in Fig. 5.9, has been seen in simulations [101]. However, the origin of this behaviour was not discussed. We believe that this behaviour is due to a gradual rippling of nanotube’s walls. At point 1 in Fig. 5.9 the outermost wall ripples without yet spreading the rippling deformation to the inner walls. As the nanotube is continually bent, more walls ripple until all walls have rippled at point 2 and there is a drop in the force. Upon retraction, the whole tube recovers from the rippling at point 3 where there is a slight increase in the force. This behaviour introduces a hysteresis that would damp an oscillating nanotube if bent past point 2, which is undesirably for many applications. From our interpretation it follows that the extent of the region between point 1 and 2 depends on the number of walls and thereby also on $t_N$. For MWNCTs with a small $t_N$ this region should thus be fairly short and thus hard to detect, but would nevertheless affect the vibrational behaviour.
5.1 Multi-walled carbon nanotubes

5.1.4 Increased wall spacing

As discussed above, the rippling deformation is elastic, i.e. the tube returns to its initial shape when the bending force is released. However, upon bending strains well past the rippling onset we have observed irreversible mechanical deformation. As shown in Fig. 5.10 the spacing between the walls seems to have increased next to the rippled region. This increased wall spacing is only seen on the compressed side of the tube, whereas the wall spacing is unchanged on the stretched side.

![Figure 5.10](image)

**Figure 5.10:** (a) MWCNT prior to bending. When bent, the tube ripples in the region of the dashed area, as shown in image (b)-(d). (b) The tube is well past the rippling onset and a localized rippling pattern has been created. (c) Upon release of the bending force, the wall spacing increases on the left side of the rippled region. (d) Upon further release the walls split up even more, and the region of this increased wall spacing grows. (e) The increased wall spacing remains after the bending force is fully released.

The structural change seems to be initiated by the rippling pattern as it gradually grows from the ripple. The increased wall spacing in this region is only possible if the
5. RESULTS AND DISCUSSION

Wall spacing in another region is reduced or if the circumference of the individual walls is mismatched, i.e. if \( d_{j+1} - d_j > 2 \times 0.34 \) nm for two adjacent walls. Another feature seen in Fig. 5.10 is that the width of the hollow part is increased in the region of the increased wall spacing, indicating that the MWCNT have an elliptic cross-section in this region. It should be stated that this change of structure was observed while illuminating the MWCNT with an electron beam of acceleration voltage 80 kV. The electron beam could facilitate the structural change by exciting electrons of the MWCNT, so that they could overcome the threshold for the structural change.

If the walls have mismatched circumferences from the growth process it could lead to a water-drop-like cross section where the inter-wall distance is locally larger than 0.34 nm [102]. In TEM-images, this is only clearly visible if the planes with the increased wall spacing are parallel to the electron beam, as shown in Fig. 5.11. The rippling might then simply transfer the locally larger wall-spacing from a side where the stress is large, Fig. 5.11 (a), to the side where the stress from the rippling is the smallest, Fig. 5.11 (b). The side with the smallest stress is the compressed side of the tube which, for our experimental configuration, means that the planes are parallel to the electron beam.

![Figure 5.11](image-url)

**Figure 5.11:** If a mismatch in wall spacing is located with planes perpendicular to the electron beam, as in (a), it will not be visible in a TEM-image. If the mismatched planes instead are parallel to the beam, as in (b), it will be visible.

If the wall spacing is locally decreased in a region not visible in a TEM-image it enables a local increase in wall spacing on the compressed side. This would be possible if there is a re-hybridization of the \( sp^2 \)-orbitals in the walls towards \( sp^3 \)-like orbitals, leading to inter-wall covalent bridges. Modelling has shown that such hybridizations occur at high pressures in nanoindented graphite and CNTs [103]. Modelling has also
shown that such inter-wall bridges can be formed in severely rippled MWCNT [104]. The bridges form where the stress and curvatures are the largest, i.e. at the sharp edges of the ripple where the planes are perpendicular to the electron beam. In these inter-wall bridges the $\pi$-orbitals of two adjacent walls hybridize to form a covalent bond. The layers should thereby be paired up, which is indeed seen in Fig. 5.10.

If there is a rehybridization of the orbitals leading to covalent bridges this will affect the electronic properties of the CNT. The region of this rehybridization could serve as a tunneling junction for electrons[104], which could be utilized in single-electron transistor applications [20, 21], but would be detrimental in applications where a high conductivity is wanted, e.g. in nano-relays.

5.2 Vertically aligned carbon nanofibers

In order to perform mechanical measurements on VACNFs, a substrate where VACNFs had been grown onto (described in section 4.2.2) was cut and glued onto a silver wire. This wire was mounted in a tip holder which was inserted in the in situ SEM-AFM instrument, see Fig. 3.13 for experimental set-up.

Force curves from 5 fibers of group A and 5 fibers of group B were obtained. SEM images of an unloaded and bent CNF, along with a $F$-$\delta$ curve, are shown in Fig. 5.12.

From these $F$-$\delta$ curves the spring constants of the fibers, $k^{\text{CNF}}$, could be obtained from Eq. 3.22 and used to calculate $E$ of the fibers. Since the fibers were tapered, their area moment of inertia, $I$, varied across their length as:

$$I = \frac{\pi (r_t + \alpha x)^4}{4}$$  \hspace{1cm} (5.4)

where $x$ is defined from Fig. 3.17, $r_t$ is the radius at the tip, and $\alpha$ is the taperdness factor defined in Eq. 4.1. From beam theory one can deduce that the deflection, $\delta$, of an elastic beam subjected to a point force, $F$, at one end is related to $F$ as:

$$\frac{d^2\delta}{dx^2} = \frac{4F}{\pi E (r_t + \alpha x)^4}$$  \hspace{1cm} (5.5)

Integrating Eq. 5.5 twice and using the boundary conditions of a cantilevered beam ($\delta(l) = \delta'(l) = 0$), the relation between the deflection at the point of the applied force can be written as:

$$\delta(0) = \frac{4Fl^3}{3\pi E r_t F b}$$  \hspace{1cm} (5.6)
5. RESULTS AND DISCUSSION

![Figure 5.12: SEM image of a CNF (a) before bending and (b) bent. (c) $F - \delta$ curve obtained by pushing an individual CNF.](image)

where $l$ is the length, and $r_b$ and $r_t$ is the radius at the base and tip respectively. Young’s modulus of the fiber can be obtained by using Eq. 5.6 along with $k^{CNF} = \Delta F/\Delta \delta$. This was done for the measured fibers and the result is shown in Fig. 5.13, where $E$ was plotted against the taperedness factor $\alpha$.

As seen in Fig. 5.13 $E$ increases with increasing taperedness. Since the taperedness is a result of deposition of amorphous carbon on the fibers during growth, more tapered fibers have more amorphous carbon deposited on them. Modelling the fibers as a homogeneous material (as was done in Eq. 5.5 and 5.6) thus yields a taperedness dependence on $E$, since the graphitic core and the amorphous carbon have different elastic moduli. By instead prescribing an Young’s modulus of $E_{core}$ and $E_{am-C}$ to the graphitic core and the deposit of amorphous carbon respectively Eq. 5.5 is rewritten.
Taperedness factor (\(a^\ast 100\)) was fitted to the 10 measured values of with a combinatorial method.

As:

\[
\frac{d^2 \delta}{dx^2} = \frac{4F}{\pi E_{\text{a-C}} \left( r_1 + ax \right)^4 - r_1^4} + E_{\text{core}} r_1^4 \tag{5.7}
\]

Integrating this equation twice and again using the boundary conditions of a cantilevered beam, the spring constant of the fiber can be expressed as:

\[
k_{\text{CNF}} = \frac{\pi \alpha^3 \beta E_{\text{a-C}} r_1}{2 (\beta^2 - 1) \arctan \left( \frac{\beta (r_2 - r_1)}{3r_2^2 + r_1^2} \right) + (\beta^2 + 1) \ln \left( \frac{(1 + \beta)(r_2 - r_1)}{1 - \beta} \right) + 2 \beta \ln \left( \frac{(1 - \beta)(r_2^2 + \beta r_1^2)}{(1 + \beta)(r_2^2 - \beta r_1^2)} \right) \right) \tag{5.8}
\]

where \(\beta = (E_{\text{a-C}} - E_{\text{core}}) / E_{\text{a-C}}\). Eq. 5.8 was fitted to the 10 measured values of \(k_{\text{CNF}}\) by finding a minimum of the variance, defined as:

\[
\Delta^2 = \frac{1}{10} \sum_{i=1}^{10} \left( \frac{k_{\text{CNF}}^{\text{calc}}(E_{\text{core}}, E_{\text{a-C}}) - k_{\text{CNF}}^{\text{meas}}} {k_{\text{CNF}}^{\text{meas}}} \right)^2 \tag{5.9}
\]

where \(k_{\text{CNF}}^{\text{calc}}(E_{\text{core}}, E_{\text{a-C}})\) is a calculated spring constant using Eq. 5.8 with a combination of \(E_{\text{core}}\) and \(E_{\text{a-C}}\) and \(k_{\text{CNF}}^{\text{meas}}\) is a measured spring constant. The variance, \(\Delta^2\), is plotted against combinations of \(E_{\text{core}}\) and \(E_{\text{a-C}}\) in Fig. 5.14.

The best fit to Eq. 5.8, i.e. the minimum of \(\Delta^2\), was obtained for \(E_{\text{core}} \approx 10\) GPa and \(E_{\text{a-C}} \approx 65\) GPa. The low value of \(E_{\text{core}} \approx 10\) GPa, compared to the \(E = 1\) TPa for perfect CNTs, can be understood from the inferred structured (Fig. 4.2) since the core consists of a graphitic cup-stacked structure, making the angle between the
5. RESULTS AND DISCUSSION

Figure 5.14: The mean square difference between the measured spring constants and the spring constants calculated using Eq. 5.8 with $E_{\text{a-C}}$ and $E_{\text{core}}$.

graphitic planes and the tube axis, $\theta$, non-zero. Hence, the graphitic layers will shear against each other when bending the fiber. For graphitic materials the shear modulus is much lower than the in-plane modulus [24]. Thereby, as $\theta$ grows the shear modulus will govern the mechanical behaviour, according to Eq. 2.8 and Fig. 2.4, and the stiffness in the axial direction will be significantly lowered.
Chapter 6

Conclusions and outlook

We have studied the mechanical behaviour of individual MWCNTs and VACNFs. The results show that the bending stiffness is very sensitive to the internal structure of the tubes. Only highly crystalline MWCNTs (grown by arc-discharge) have a Young’s modulus close to the ideal value of about 1 TPa. MWCNTs with a lower crystallinity (grown by CVD), have a much lower Young’s modulus, about one order of magnitude smaller. For VACNFs, where the graphene layers are not parallel to the fiber axis, the value of Young’s modulus is yet an order of magnitude lower.

When CNTs are bent above a critical strain they will exhibit localized deformations, i.e. they ripple or buckle. This greatly reduces the bending stiffness, which is detrimental for applications requiring a high bending stiffness over a large deflection range, e.g. nanorelays. Our studies show that the critical strain is highly dependent on the normalized wall thickness of the tubes, as the inner tubes supports the outermost ones where rippling would otherwise commence. This supporting effect gives a variation in the critical strain by up to a factor of three for tubes with the same outer diameter.

Tubes with a higher defect density have a larger critical strain for rippling and also possess a larger relative post-rippling stiffness, compared to tubes with high crystallinity. However, the absolute stiffness in the rippled phase is still lower than for highly crystalline tubes. The construction of nanorelays has been hampered with problems of reversibility, as the nanotube tends to stick to the drain electrode once it has been attracted there. Most studies where nanorelays were manufactured have used CVD-grown tubes or CNFs, as they are more easily incorporated in the device structure. Our results show that these materials are unsuitable for nanorelays due to their low...
6. CONCLUSIONS AND OUTLOOK

stiffness. Instead, highly crystalline tubes, for instance grown by arc-discharge, should be used with a small inner diameter which will allow for an extended deflection range. In the future it would also be interesting to study if there exists defects, as suggested by modelling like cross-linking of layers, which could increase the critical strain and post-rippling stiffness, without lowering the stiffness prior to rippling.

We have observed local variations of the inter-wall spacing in nanotubes after bending. The increased wall spacing is very intriguing and has not yet been studied in detail. For future work, the geometry of the experimental setup could be changed so that the CNT can be rotated inside the TEM, before and during bending. This could reveal whether or not the increased wall spacing was present on another side, not visible in TEM, before the rippling. The influence of the increased wall spacing on the electrical properties would also be interesting to study.

The electrical and thermal properties of the CNT are very interesting for applications. While the buckling and rippling should have large influence on these properties, it is very hard to study with traditional techniques. With further developments of TEM in situ tools, using multiple probes and electrically conductive cantilevers, it will hopefully be possible to characterize these properties in the future.
References


REFERENCES

REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


Mechanical behaviour of carbon nanostructures

Carbon nanotubes (CNTs) have extraordinary mechanical and electrical properties. Together with their small dimensions and low density, they are attractive candidates for building blocks in nanoelectromechanical systems (NEMS), and many other applications. In this thesis the mechanical behaviour of individual CNTs and vertically aligned carbon nanofibers has been studied by performing force measurements inside electron microscopes. We have found that the mechanical behaviour is very sensitive to the defect density and the internal structure of the CNTs. The extraordinary properties are only attained by defect free CNTs and quickly deteriorate if defects are introduced to the structure. Mechanical deformations also alter these properties. Single-walled CNTs behave similarly to drinking straws when bent, i.e. they buckle, while the inner tubes of multi-walled CNTs prevent buckling. Instead a more distributed rippling pattern is created for multi-walled CNTs. Both these deformation behaviours will cause an abrupt drop in the bending stiffness, which is detrimental for many applications. The findings in this work will have implications for the design of future NEMS.