Determining the interwall spacing in carbon nanotubes by using transmission electron microscopy

Undersökning av väggavstånden i kolnanorör med hjälp av transmissions-elektronmikroskopi

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Abstract

The interwall spacing of multi-walled carbon nanotubes has an effect on their physical and chemical properties. Tubes with larger interwall spacing - compared to the spacing where the carbon atoms are in their natural distance to each other - are for instance expected to be mechanically less stable. Considering the MWCNT interwall spacing’s dependence on the tube size, three interesting previous studies with slightly different conclusions can be found. All of them conclude an increase of the interwall spacing with a decreasing tube size. We describe their analysis procedure, compare them to each other and to our own measured data.

In the beginning of our analyses, we determine the expected inaccuracy for measured distances out of TEM images being up to 10 % and we show the impacts of the TEM’s defocus, a powerful setting in TEM imaging. Finally, we suppose that the interwall spacings are not as strongly varying as one previous study concludes, but our analyses are relatively in harmony with the two other studies. The interwall spacings from tubes with an inner diameter larger than 5 nm are relatively constant within the whole tube. Furthermore, it appears that the middle spacings (excluding the outer- and innermost ones) show values that are most consistent with the interlayer spacings of turbostratic graphite. In underfocused images, the outer- and innermost spacings tend to have values being slightly smaller than the middle ones from the same tube.

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The researched nanotubes are denoted as Tube 1-4. Images of them are shown in the appendix.

Tube 1  One of the researched nanotubes (‘CNT 3100’)
Tube 2  One of the researched nanotubes (‘CNT 3100’)
Tube 3  One of the researched nanotubes (‘CNT 3100’)
Tube 4  One of the researched nanotubes (iron filled; ‘HP2’, manufactured by pyrolysis of ferrocene)
1. Introduction

1.1 General Background Carbon Nanotubes

Carbon nanotubes (CNTs) are a tubular structure of carbon, shown in Figure 1. The carbon’s chemical bonds are the same as they are in graphene. Although (hollow) tubular carbon filaments were actually observed already in the 1950s, the large scientific community paid attention to them after a publication by Sumio Iijima in 1991, in which he clearly characterized them (Monthioux & Kuznetsov 2006). CNTs can be thought of as rolled-up sheets of graphene. In the most basic case, they come up with one wall (SWCNT), but it is possible that a tube consists of two or even more walls. Those walls are disposed coaxially, as seen in Figure 2. This rolled-up graphene sheet only illustrates the tube’s structure and is not a possible manufacturing process. One important parameter of those MWCNTs is the distance between adjacent walls. Some previous studies of this interwall spacing show values in the range of 0.32-0.35 nm, with the suspicion of being dependent on the tube’s size (Kharissova & Kharisov 2014). A value for the spacing of 0.344 nm seems reasonable as this is as well the interlayer spacing of turbostratic graphite (Inagaki et al. 2013). The major goal of this work is researching this interwall spacing.

![Figure 1](Internet source 1 n.d.)

![Figure 2](Internet source 2 n.d.)
Depending on the graphene’s curl (or how the graphene sheet was orientated), a CNT’s wall can be classified in three different structures: armchair, chiral and zigzag, which are shown in Figure 3.

![Figure 3](image)

**Figure 3** CNTs in different structures: armchair (top), chiral (middle) and zigzag (bottom).

Because CNTs are a rather new material, their applications haven’t become common in everyday life yet. Considering the last years’ trend of publications, issued patents, and production capacity, this will very probably change in the next years, as demonstrated in Figure 4 (De Volder et al. 2013).

There is a general consensus that CNTs will have a great future that will permit big developments.

![Figure 4](image)

**Figure 4** CNTs’ trend in publications, issued patents and production capacity during the last years and some important achievements.
Some possible application fields of CNTs are batteries, supercapacitors, solar cells, and water filters (De Volder et al. 2013). Figure 5 allows a brief impression of two further possible future applications. Some people think that with the help of CNTs, one day it will be possible to create a rope that is strong enough to make the future project of a space elevator possible. Another research topic is CNTs serving as a hydrogen storage, using the tubes’ capillary effect. It is said that they may lead to a new superior storage technology for hydrogen fueled vehicles if improvements in their purification and alignment are achieved (Dillon et al. 1997).
1.2 Motivation and goals

It is clearly imaginable that the nanotubes’ interwall spacing has an effect on their physical and chemical properties. Tubes with larger interwall spacing - compared to the spacing where the carbon atoms are in their natural distance to each other - are for instance expected to be mechanically less stable. A spacing’s dependence on the number of walls, the tube’s diameter or the spacings’ index might be therefore quite important for explaining the tubes’ properties and developing further applications.

Considering the CNT interwall spacing’s dependence on the tube size, three interesting previous studies with slight different conclusions can be found. Commonly, they show an increase of the interwall spacing with a decrease in the tube’s size.

In order to find the spacings in TEM images as accurate as possible, we need to deal with the issues of the images’ defocus. A TEM’s focus is not comparable with a photographic focus in which the researched object just gets blurred if it is out of focus. In TEM imaging, the defocus is a powerful setting as it might hide some information or details but in the same way intensify some others. Figure 6 shows an example of how the defocus value influences the image as Fresnel fringes appear.

Figure 6 Fresnel fringes, seen in TEM images of Tube 3; a) an underfocused one and b) an overfocused one.

Therefore, we suspect that in some cases it could be insufficient to make the measurements out of only one single image. Our first goal is to show some appearing issues due to the defocus and we will propose a procedure to achieve information from TEM images as trustworthy as possible. The next point is to set an expected accuracy of measurements with our procedure of analyzing contrast profiles. Afterwards, we research if the distances in TEM images are influenced by the defocus. In the end, there will be our results on the interwall spacings compared with the previous studies and an outlook regarding an even more improved analysis in this topic.
1.3 Previous studies

“Size Effects in Carbon Nanotubes,” (Kiang et al. 1998)

This is the earliest of the three presented studies. The authors start with a brief review of previous studies, which measured a varying CNT’s intershell spacing within 0.34 nm to 0.375, and they mention a possible dependence on the tube size that will be studied. Then, they research two tubes in a TEM image and take values for a third tube out of another reference (Sun et al. 1996) - this paper was published by three common authors. Each data point implies being an average of 5 measurements with an error-reduction to 3%.

It should be noted that what they call ‘diameter D’ (see x-axis) should be understood as the individual wall’s diameter. This denotation might cause some confusion if a tube’s diameter is understood as its outer diameter (the outermost wall’s distance to the tube center, which is what we understand by calling it a diameter).

In general, the displayed TEM image has a good quality and the procedure of taking an average of 5 measurements seems adequate. On the other hand, it is in a way risky to base the whole analysis on only two images, especially if the researched tubes possess such a different number of walls.

They present an empirical exponential function as being the best fit to the data:

$$\hat{d}_{002} = 0.344 + 0.1e^{-D/2} \quad \text{for } D \geq 0,$$

where the authors call D the “tube’s inner diameter”. More suitable may be “individual wall’s diameter.”

For tubes with a centrum-distance of more than 10 nm, they describe a roughly constant spacing of about 0.344 nm, the same spacing as that of turbostratic graphite layers. Furthermore, the increase in the $d_{002}$-spacing with decreasing tube size is described as physically reasonable as
“the repulsive forces of the graphene basal planes between adjacent tubes are larger for smaller diameter tubes, owing to their larger curvature, which perturbs the geometric and electronic structures relative to a planar graphene sheet”.

“Radial Corrugations of Multi-Walled Carbon Nanotubes Driven by Inter-Wall Nonbonding Interactions,” (Huang et al. 2010)

**Figure 8** The calculated interwall spacings of zigzag MWCNTs with a different number of walls. The spacing of the innermost wall is taken as its radius. The dashed line indicates the original spacing of relaxed zigzag MWCNTs.

The authors of this paper performed “large-scale quasi-continuum simulations on the stable cross-sectional configurations of MWCNTs”. This is done by calculations that consider the interwall vdW interaction, the out-of-plane bending energy, and the in-plane stretching energy. In general, they present a slight decrease in the inter-wall spacing from inner to outer walls. Except for the 25-walled MWCNT, this even happens monotonically. As the first (the highest) data point in **Figure 8** is the innermost wall’s radius and not a classic interwall-spacing, the values vary between about 0.34 nm and 0.355 nm.
For Figure 9, we calculated the individual wall diameters for the 10-walled CNT out of the presented values. By doing this, we can compare those theoretical values with the empirical equation from (Kiang et al. 1998). We see that for individual wall’s diameters larger than 3.0 nm, both studies are in a way similar with a difference of less than 0.02 nm. For smaller distances, their difference gets larger (up to about 0.05 nm).

Figure 9 Comparison of the interwall spacings according to the equation from (Kiang et al. 1998) and the calculated values from (Huang et al. 2010) for a 10-walled CNT.
“Diameter dependence of interwall separation and strain in multiwalled carbon nanotubes probed by X-ray diffraction and Raman scattering studies,” (Singh et al. 2010)

This Indian research team published a paper in 2010 describing a connection between a carbon nanotube’s outer diameter and its d_{002} / interwall spacing. This paper differs from the previous ones in this aspect, as it describes a varying average wall spacing between different CNTs.

According to their description, they took five different samples for the analysis. Each of them was a bundle of CNTs with a different tube’s diameter range (specified by the supplier; <10 nm, 10–20 nm, 10–30 nm, 20–40 nm, 40–60 nm and 60–100 nm). It should be noted that in this paper the “diameter” denotes the tubes’ average outer diameter in each sample. For each sample, the interwall spacing was determined in two different ways.

For one measurement, an average diameter was estimated by analyzing the TEM images of 20 nanotubes. Then, apparently only one measured interwall spacing per sample was recorded. This single measurement, as well as the tube’s doubtful image quality, is shown in Figure 10 (g,h,k). Therefore, the achieved data points show the interwall spacing correlating with an average diameter, but not the respective tube’s diameter.
In a second measurement, they determine each sample’s average interwall spacing by XRD analysis. Those XRD-spacings are slightly higher than the ones out of the TEM images. Regarding the XRD-values, the authors concluded here as well an exponential function being “the best fit”:

\[ d_{002} = 0.345 + 0.37 e^{-D/14.4} \]

where D is the tube’s outer diameter.

Unfortunately, the authors don’t discuss the accuracy of those data points. As far as they describe the XRD analysis, they base their conclusion on a very slightly shifted (002)-peak (from 25.7° to 26.2°). All in all, their conclusion’s validity is in question.

The authors believe the increased interwall spacing at a tube’s smaller diameter is caused primarily by the high curvature and thus the high strain in the lower diameter nanotubes, which might cause charged defects in the walls and therefore causes coulombic repulsion. Furthermore, they explain large diameter MWCNTs have a higher walls’ interaction due to an implied higher number of walls, causing a decrease in the interwall spacing.

Interestingly, they also make a statement about the interwall spacing’s variation within one CNT, stating: “a careful analysis of the HRTEM images reveals that the inner wall separation is about 3 % higher than the outer wall separation for a diameter up to 60 nm. However, for very large diameter (80-100 nm) nanotubes the wall separation first decreases as one moves from the innermost wall to the outer walls and then it again increases near the outermost walls that may be due to the structural defects at the outer walls of the MWCNTs as seen from HRTEM images (not shown).”
Chapter 2 - Technical Background

2. Technical Background

2.1 Growth techniques

2.1.1 Arc discharge

![Sketch of an arc discharge construction](Image)

Figure 12 Sketch of an arc discharge construction. (Internet source 12 n.d.)

The arc discharge process has its origins in the synthesis of fullerenes. For the production of carbon nanotubes by this procedure, a high DC current flows between a graphite anode and cathode. The electrodes are surrounded by a plasma of helium gas with temperatures of up to 4000 K. A sketch of this is shown in Figure 12. The current causes evaporated carbon atoms within this plasma, which will build carbon nanotubes (among other depositions) on the electrodes.

This process has been developed as an excellent method for producing MWCNTs and SWCNTs in high quality. The result of the created CNTs can be influenced by the choice of a metallic catalyst / precursor on one of the electrodes, the pressure of the inert gas, and the arcing current. A disadvantage is that only relatively small amounts of CNTs can be produced this way. (Dresselhaus et al. 2001), (Mishra 2013)

2.1.2 Laser ablation

Inside a furnace heated up to a temperature of approximately 1200 °C, a powerful laser shoots pulses on a graphite target, which evaporates carbon atoms out of it. By having a flow of inert gas, e.g. argon, the evaporated carbon moves to a cooled collector, e.g. out of copper, at the end of the furnace. In a way similar to the arc discharge process, carbon nanotubes will be built among other depositions at the tip of the collector. (Harris 2009)
2.1.3 Chemical Vapor Deposition (CVD)

![Diagram of CNT growth mechanisms]

**Figure 13** The two widely-accepted CNTs’ growth mechanisms; a) the tip-growth model and b) the base-growth model. (Kumar 2010)

In the CVD-process, carbon nanotubes are made by flowing a hydrocarbon gas past a catalyst material. These metallic catalysts are heated up to temperatures of about 500°C to 1100°C or even higher for the special “plasma enhanced CVD”. The main advantage of this process is the possibility of producing large amounts of CNTs relatively easy. Important parameters are the used hydrocarbons, the used catalysts, and the oven temperature.

The growth mechanism is based in general on the dissociation of hydrocarbon molecules with the help of the catalyst. Dissociated carbon atoms dissolve in the metal nanoparticles until they are saturated. The subsequent precipitation of sp²-hybridized carbon leads to the formation of tubular carbon solids. The tube’s growth could happen either by the tip- or the base-growth model which is shown in **Figure 13**. The reason why the tubular shape is favored is that in this formation no open edges or dangling bonds are existing, giving it the lowest energy. (Dresselhaus et al. 2001), (Mishra 2013)
2.2 TEM

2.2.1 General Functionality

An electron beam is formed by a system containing an electron source and electron accelerators. This beam is adjustable by condenser lenses that are electromagnetic coils, hitting an area of a thin specimen being researched. A TEM’s sketch is shown in Figure 14. This electron beam might be parallel or convergent when hitting the specimen, depending on the TEM’s mode. For our imaging, we expect the beam to be parallel. Electrons are passing the specimen either without any interaction, or they hit matter and scatter, elastically or inelastically. Elastically scattered electrons just change their original direction because of Coulomb forces when entering an atom’s electron cloud. Depending on the proximity to the nucleus, the scattering angle varies, see Figure 15. In general, the higher the atomic number of the interacting matter, the stronger the attractive force from the nuclei, resulting in a higher interaction and causing an increase in the average scattering angle. This influence of the atomic number finally allows to see a mass contrast image. Alternatively, if observing a crystalline sample, the electron wave interacts with the specimen as a whole and diffraction occurs.
Inelastically scattered electrons might cause the appearance of e.g. X-rays and Auger-electrons. Those might divulge very useful information about the specimen but their research is not part of the usual TEM imaging.

After hitting the specimen, the electron beam will pass lenses and apertures (shown in Figure 16). The beam’s focus may be changed manually. This defocusing will be used later in our research. High angle scattered electrons will be excluded. With the help of the two apertures, limitations can be set, both in real and diffraction space. Depending on the chosen TEM’s mode (different strength of lenses) either the real image or a diffraction pattern will be obtained.

All this happens in a vacuum, as the better the present vacuum is, the longer is the time that contaminants will need to form layers on the substrate which might decrease the quality of the recorded images. Finally, the electron beam impinges on a fluorescent screen or into the image recording system and a TEM image is obtained.
2.2.2 Objective Aperture

Changing the objective aperture is another important configuration of the TEM to influence the images’ resolution. The aperture’s size controls the collection of the transmitted beam and the diffraction spots, shown in Figure 17. In general, the more beams that are selected, the higher the image’s resolution will be. (Williams & Carter 2009), (Bendersky & Gayle 2001)
A selection of both the direct and diffracted beams happens by choosing a sufficient big aperture or even none at all and it allows the best resolution as it improves the phase contrast. By choosing a small aperture, information at a larger distance from the central diffraction spot – including higher spatial frequency information – will not be contained in the image. On the other hand, a smaller aperture is useful for imaging thicker samples which tend to cause scattering in a large angular spread. (Hafner 2011)

**Figure 18** shows example images of the same MWCNT taken with different objective apertures. By using the smallest aperture with excluding most of the scattered electrons, the information of the individual walls is not contained in the image anymore.

![Figure 18 TEM images of the same MWCNT by using different objective apertures. The images a-d) go from the biggest to the smallest aperture, being a) OA1, b) OA2, c) OA3, d) OA4. (Jackman 2014b)](image)
2.3 Defocus Setting and Fresnel Fringes

In TEM imaging, the defocus can be used as a powerful tool for changing contrast conditions with the purpose of imaging matter that would look different or wouldn’t be visible at another defocus. This works, for example, for voids or small gas-filled cavities as those don’t scatter electrons but they become visible by the appearance of so called Fresnel fringes. As carbon matter scatters electrons, in general this effect would not be necessary to image it, but it is an effect which improves the imaging of graphite and CNTs as well. An illustration of Fresnel fringes is shown in Figure 19 with the help of an underfocused, a focused, and an overfocused TEM image. The focused one, around zero defocus, shows the lowest contrast. (Hafner 2011)

![Figure 19 Example for Fresnel fringes at different defocuses: underfocus, zero defocus, overfocus.](image)

Although the focus setting can be very useful for amplifying and imaging some certain information, it demands also attentiveness. Especially in analyzing only one single TEM image, sometimes Fresnel fringes could be misinterpreted as a shell structure. Later, those appearing artifacts will be important as CNTs can show additional walls (“ghost walls”) at certain defocuses.
2.4 The Contrast Transfer Function and Scherzer Defocus

In order to briefly discuss the details of the contrast theory, the so called transfer function needs to be established. This function is pictured as $T(u)$ in Figure 20. Here $u$ denotes a reciprocal lattice vector, the spatial frequency for a particular direction. $u_1$ defines the function’s first zero. Negative values for $T(u)$ result in a positive phase contrast which would image atoms dark against a bright background. Positive values for $T(u)$ result in a negative phase contrast and would image atoms bright against a dark background. If $T(u)$ has the value 0, it would cause this value of $u$ to not have any detail in the image. It is desirable to have $u_1$ as large as possible. The higher it is, the more information is shown ‘truly’ in the image.

The transfer function can be called contrast transfer function (CTF) if the specimen acts as a weak-phase object. Plots of CTFs are shown in Figure 21 in which their typical oscillations are visible. The CTF’s passband is related to the width of the very first dip (see Figure 21a). It should be as large as possible to be the closest to the ideal transfer function. There is one defocus where this passband is biggest, the so called Scherzer defocus. This Scherzer defocus is always negative (underfocused image) and therefore in general it happens that matter boundaries appear as bright fringes. (Williams & Carter 2009), (Hafner 2011)

![Figure 20](image-url) The ideal form of the transfer function. $u_1$ defines the function’s zero.
Figure 21 CTFs with an envelope function. The envelope function acts as a virtual aperture. a) The CTF at a moderate defocus; b) The CTF at Scherzer defocus. It has the fewest zeros and the broadest passband, providing a good transmittance and a dark contrast from the material.

A proper description and the mathematical background of the Scherzer defocus and the Fresnel fringes is not within the scope of this work and we refer to (Williams & Carter 2009). Two TEM images of one CNT at different defocuses are shown in Figure 22. It should just be noted that there exists one certain defocus value (Scherzer defocus) where TEM images show the most information possible, which can be interpreted instinctively with the naked eye.

Figure 22 Tube 1 at two different defocuses; a) image close to the zero defocus (original defocus +20 nm); b) image close to the Scherzer defocus (original defocus -20 nm).
2.5 Image artifacts and delocalizations

In general, one needs to be careful when beholding TEM images. Figure 23 shows an interesting comparison with the help of a regular photography. A person named Hayes took this photograph and said “when we see this image we laugh” because we know its true background information, “but when we see equivalent (but more misleading) images in the TEM, we publish!”. Therefore, one should beware of artifacts which might appear in TEM images. (Williams & Carter 2009)

![Figure 23](image)

**Figure 23** This photography of two rhinos is an example of how a circumstance could be adopted wrongly by just looking at one single picture. Only by this picture, one could easily recognize a two-headed rhino.

As it is already shown in Figure 6, in different defocuses we observed slightly different images. The paper (Hayashi et al. 2006) is showing and discussing this appearance. The authors simulated TEM images of carbon nanotubes and especially compared a 5-walled and a 6-walled MWCNT, their only difference is that the 5-walled one is missing a 0.4 nm tube in the core. The simulated images and their contrast profiles are shown in Figure 24. The images show dark lines appearing in the core of the 5-walled MWCNT, although there isn’t supposed to be any tube. The authors describe that the real tube’s contrast becomes lower with an increasing number of the tube’s walls. During this, the ghost wall’s contrast remains the same. On account of this, if the ghost-tube’s contrast is high enough, the wrong number of walls for a tube could be estimated if only one image is considered. Accordingly, they suggest to avoid this problem “by obtaining a series of images changing the defocus condition in a stepwise manner”. (Hayashi et al. 2006)

As we didn’t research nanotubes with such a small inner diameter, this case is slightly different from ours. However, the cause and the origins are the same as we had by seeing the appearance of ghost walls, shown in Figure 25. In the image at defocus -80 nm, one could estimate the CNT has 8 walls, but that’s wrong. It has 7 as some other defocused images show, e.g. the one at -20 nm.
Figure 24 Simulated images and corresponding contrast profiles (indicated by the sections of the images) of MWCNTs: Outer Diameter and the (outer) walls are exactly the same, except (a) is without a 0.4 nm tube and (b) is with a 0.4 nm tube in the core.

**Annotation:**
All over this work, in the contrast profiles, relatively low values refer to a dark area in the correlating integration section and relatively high values refer to a bright area.

Figure 25 TEM images of Tube 2; a) defocus -80 nm; b) defocus -80 nm, zoomed in, showing 8 walls; c) defocus -20 nm, zoomed in, showing 7 walls.

To sum up, the point is that both CNTs and graphite consist of several walls or layers, respectively. Both are more or less seen as parallel lines in TEM images. At some defocus values it is possible that Fresnel fringes appear which could be interpreted wrongly as walls or layers.

Other simulated images showing this case are shown in (Wang 2003) and a proper explanation about delocalizations or “FEG TEMs and the information limit” can be found in (Williams & Carter 2009).

To handle with this problem, we propose a procedure of taking 10 images of the same nanotube within the range of being blurred because of underfocus and being blurred because of overfocus. With the help of those 10 images, it should be possible to determine which walls are real and which are ghost walls.
3. Experimental

3.1 The used TEM and our specific settings

We imaged the samples in a JEOL (JEM 2100) TEM equipped with a LaB₆ cathode and a digital camera from Gatan (SC1000 Orsius). The acceleration voltage was set at 90 kV. A higher acceleration voltage would in general lead to an improved image quality but then the probability of damaging the nanotubes gets higher. Therefore, we set a smaller voltage because the beam hit our samples for a relatively long time while we took the defocus series. (Jackman 2014a)

The TEM’s calibration and accuracy was checked by looking at a gold sample. One of the analyzed images is shown in Figure 26. Out of 6 analyses (6 gold particles in two images, consciously different particle’s orientations), the measured distances are on average 3.0 % larger than they should be. This 3.0 % excess is relatively good. Therefore, the instrument’s general calibration was not changed. Only for the conclusions in chapter 5 our measured values are corrected by this excess. A more detailed description of this check can be found in the appendix.

![Figure 26](image)

**Figure 26** One of the analyzed images of the gold sample. The cognizable lattice fringes are mostly belonging to the (111) plains.

3.2 Analysis procedure and software

For measuring distances in TEM images, we created contrast profiles of certain sections. An example of a contrast profile is shown in Figure 24. They basically show a dark-bright proportion along a line, integrated across a certain width. By choosing a section with a width and not just a single line, we achieve a reduction of error caused by noise in the image. In those contrast profiles, walls or layers can be seen as dips. With the help of the software Origin, we chose an interval on the x-axis in which the software creates a Gaussian fit (least square) to the selected dip. Figure 27 and Figure 28 show this Gaussian fitting for contrast profiles of TEM images of the same tube at two different defocuses.
Figure 27 Contrast profile of tube 3 at defocus -60 nm. The yellow window represents the chosen interval for the Gaussian fits. The value “xc” in the dip’s information denotes the position of the dip center on the x-axis. The fits are shown as the blue lines. The correlating TEM image can be seen in the appendix, Figure 57a.

Figure 28 Contrast profile of tube 3 at defocus -30 nm. The yellow window represents the chosen interval for the Gaussian fits. The value “xc” in the dip’s information denotes the position of the dip center on the x-axis. The fits are shown as the blue lines. The correlating TEM image can be seen in the appendix, Figure 57b.
3.3 Sample Preparation

Except the specimen with iron-filled CNTs, both the graphite and the CNTs specimens were prepared specially for this work. Some powder of the graphite (‘Aldrich Nanocarbon’) was put together with Ethanol in a small container. It almost didn’t go into solution. To improve the dissolution, the sample was put into an ultrasonic bath whereas its receptacle was filled with water. The graphite sample spent 5 minutes in the ultrasonic bath before it was finally put onto a TEM specimen grid. Exactly the same procedure was done with the nanotube sample (‘CNT 3100’) except the fact that this container was 15 minutes in the ultrasonic bath. Another specimen of nanotubes which spent only 5 minutes in the bath was abandoned because it had too few useful particles.

**Annotation:**
Within this work, only TEM images of CVD-grown carbon nanotubes are researched.
4. Results

4.1 Measuring Accuracy

As already described, the spacings’ measurements are taken with the help of a contrast profile of a chosen section within a TEM image. This first of all allows the general expected measuring accuracy with this procedure to be determined. Afterwards, impacts of a possible contrast profile section’s tilt and of the chosen objective aperture are researched.

4.1.1 Determining the wall’s dips in contrast profiles

Typical contrast profiles and Gaussian fits are shown in Figure 27 and Figure 28, whereas the former shows a good quality profile and the latter shows a less smooth profile.

From our experiences in analyzing the contrast profiles, the dip’s central position (procedure described in chapter 3.2) can be found rather accurately for good quality profiles, but in general for most of the profiles the dip’s position can vary within a range of up to three pixels. With a pixel size of 0.023 nm (at a magnification of x600k), the error is in a range of 0.069 nm (±0.035 nm) which means an error of ±10% (regarding a spacing of 0.35 nm).

This error of 10 % represents the inaccuracy of one single measurement. In some following analyses, when an average of several measurements is taken, the standard deviation of those measurements will be taken as the value’s variance and replaces this contrast profile-Origin error.

In addition, it may happen that a dip is not well defined at all (seen in the orange circle in Figure 29). In those cases, the possible error could be far larger. There are two possibilities to deal with this issue: (1) It may be possible to set the dip’s choice more accurately with the help of comparing several profiles to distinguish which dip should be a wall. (2) If the Gaussian fit looks like it might not be suitable at all, then this data point might be excluded from the further analyses. As one data point would be lost by this, it should be only done if the uncertainty is very large.

Figure 29 Example of a difficulty in determining a wall’s dip in a contrast profile; a) TEM image of the correlating tube (Tube 1) with the marked section used for the contrast profile; b) Correlating contrast profile, the uncertainty of choosing the wall’s true dip among three slight dips can be seen in the circled area.
The detailed analysis of two different sections of a graphite particle is shown in the following. The two sections cover several layers what allows to look at their spacing average. Additionally, analyzing two different sections allows to check the values’ validity. By comparing different defocuses, this impact on the image and the measured spacings can be seen.

**Figure 30** The images show the upper and the lower analyzed graphite’s section; a) at defocus -100 nm; b) at defocus -200 nm.

**Figure 31** Parts from the correlating contrast profiles of some graphite layers, shown in Figure 30. The blue lines are the Gaussian fits; a) from the lower section in Figure 30a; b) from the lower section in Figure 30b.
Figure 32 Graphite’s interlayer spacing, the two lines per graph refer to the two analyzed sections per image, seen in Figure 30; a) at defocus -100 nm, b) at defocus -200 nm.

Annotation:
The interlayer or -wall spacing index 1-2 denotes the (relatively) outermost spacing, from both graphite particles and CNTs. The index 2-3 denotes the second outermost spacing, and so on.

In Figure 32a, the first data points (index 1-2) of both sections are different from the other ones’ average. Here, this difference is relatively large but in general it’s identifiable that the outermost spacings show slightly smaller values for certain defocus values (this circumstance is investigated more detailed in chapter 4.2).

Although a procedural inaccuracy of 10 % was determined earlier, Figure 32a shows that with good quality images it is possible to get consistent results with a smaller inaccuracy. In the innermost layers (neglecting the data points 1 and 2), the maximal variation is only about 3 %. Apparent in Figure 32b, with less good quality images (in this case a highly underfocused example), less consistent values are received. The results are fluctuating within a range of 0.05 nm which let assume a variation of 7 %. These variations are affirming the described procedure-error of 10%.
4.1.2 Tilt of chosen section for the contrast profile

We can determine that it is sufficient to put the sections of the contrast profiles by naked eye. Different section’s widths and tilts were analyzed, described in chapter 8.3 in the appendix. The analyses show that for sections with a width of up to 100 pixels (2.3 nm), there is no identifiable change due to a section’s tilt as long as it doesn’t exceed 4 degrees. And by our experience, a tilt of less than 4 or even less than 2 degrees is feasible to be made by the naked eye.

4.1.3 Impact of the chosen objective aperture

Different walls of our researched tube are best identifiable with the 2nd largest aperture, as without aperture the contrast profiles show dips and peaks but they are difficult to identify. With the smallest (4th largest) aperture the single walls are not visible, there are just two ‘walls’ which could be seen as the outer- and innermost wall (seen in Figure 18). Therefore, for checking the aperture’s impact on the measured spacings, Figure 33 shows the “multiwall thickness” depending on the defocus. The multiwall thickness denotes the distance between the outer- and the innermost wall.

![Figure 33 Multiwall thickness by different objective apertures and defocus values; the correlating CNT has 9 walls, the dashed line (2.75 nm) indicates the expected thickness by 8 spacings and 0.344 nm per spacing.](image)

Interestingly, Figure 33 shows almost exactly the same trend for the 2nd and 3rd largest aperture by defocusing, but with a shift of about 5 % between each other. Considering the inaccuracy, what the “no aperture”-trend affirms, an impact of the OA can’t be identified. However, it can at least be concluded that the aperture’s change doesn’t have any impact on spacings larger than being within the inaccuracy.

Summarizing, the analysis-errors of up to 10 % that were introduced in the beginning can be affirmed. It’s valid for most TEM images as long as the quality is not clearly bad. A smaller inaccuracy could be obtained by analyzing good quality images and taking an average of several measurements.
4.2 Impact of the defocus on TEM images

4.2.1 Artifacts

We recall the situation shown already in Figure 25 where a different defocus changed a tube’s apparent number of walls in TEM images. Following, a short comparison of contrast profiles can be seen in Figure 34, the correlating TEM images are in Figure 35. The profiles’ change due to the defocus is shown there, until finally a ghost wall’s dip is visible in the profile. An even more detailed comparison can be found in chapter 8.4 in the appendix.

It should be noted that the defocus value 0 nm is just a relative value configured by the person handling the TEM. Although it was attempted, it’s not possible to ensure that an image was perfectly in a zero defocus.

Regarding the expectations of the appearance of Fresnel fringes, at zero defocus there shouldn’t be any fringe next to the outermost wall. In most of our TEM images at zero defocus, however, there was still a bright fringe (for example in Figure 34c). When moving to overfocus values, usually the CNT’s structure tended to disappear completely.

![Figure 34](image.png)

Figure 34 Contrast profiles of Tube 2 (partially, only outermost part) at three different defocuses, a) -100 nm, b) -40 nm and c) 0 nm. The bright fringe changes in a way which causes at high underfocus a ghost wall next to the outermost wall. A more detailed comparison is shown in Figure 65 in the appendix.
4.2.2 Defocus’ impact on measured spacings

What we see out of the TEM images, made at different defocuses, is a changing of the fringe that is positioned next to a tube’s outermost wall. This one is supposed to be bright if underfocused, almost not existing if focused and dark if overfocused. Due to this fact and the way we make our spacing measurements (out of contrast profiles), it is a valid question if the walls / dark lines close to the fringe beam are in their position affected by this beam and hence by the defocus value.

Therefore, the next step is to consider this defocus’ impact on the measured spacings. It is researched if the measured spacings are generally influenced by the image’s defocus value. This happens first by looking at the average spacings of three graphite particles and afterwards by looking at three CNTs (one is an iron-filled CNT). Within both categories, first the impact on the average values is checked. The outermost layers or walls are consciously excluded. Afterwards, the spacing’s dependence is checked while considering both the defocus and the spacing’s index.
Impact on graphite’s spacings

Figure 36 shows TEM images of two graphite particles. Out of those and out of images at different defocuses (not shown), interlayer spacings are measured and shown in Figure 37.

It must be mentioned that the marked sections chosen for the contrast profiles (for example the ones shown in Figure 36) are not exactly in the same position for all defocuses. As the section were chosen again for every image, they might have slightly different positions. Regardless, they are at least more or less in the same position and therefore give an idea of where the spacings were measured.

Figure 36 TEM images of the two researched graphite particles and the sections chosen for the contrast profiles a) defocus -100 nm, magnification x400k; b) defocus -100 nm, magnification x600k.

Figure 37 Average values of graphite’s interlayer spacing for two different graphite particles, dependent on the defocus.

The obtained average spacing values fluctuate around 0.370 nm within about ±3 % (±0.01 nm) for most of the defocuses. The standard deviation is smallest for slight negative defocus, at -50 nm and -100 nm, which is close to the Scherzer defocus, and it gets extraordinarily high at defocus 0 nm and +50 nm.

Annotation:
The spacings shown within this chapter are not corrected by the 3.0 % excess. Therefore, it should be noted that a spacing value of 0.36 nm equates a value of 0.35 nm.
Figure 38 shows a TEM image of another graphite particle. First, the average values of the middle layers’ spacings – excluding the outermost ones – are determined (Figure 39). After that, all layers and their individual positions are taken into account (Figure 40 and Figure 41).

![TEM image of graphite particle](image)

**Figure 38** Thin graphite particle at defocus +50 nm. Its thickness allows to consider as well the individual layers’ positions.

![Graph showing average spacings](image)

**Figure 39** Average spacings (4 spacings) of the thin graphite particle, dependent on the defocus value.

Those average values vary between 0.36 and 0.37 nm. Interestingly, at a defocus value of 0 nm, the single measurements almost didn’t vary at all.

The exact averaged spacing at defocus 0 nm is (0.360 ± 0.013) nm. Considering that a TEM instrument’s excess of 3.0% was proved, the spacing 0.360 nm comes up to 0.349 nm which is very close to the spacing value of turbostratic graphite, 0.344 nm.

It can be concluded that the defocus values shown in Figure 39 are shifted compared to the defocus values shown in Figure 37. Such a shift is possible because the defocus values should be seen as relative and not absolute values.
Figure 40 Interlayer spacings of the thin graphite particle, dependent on the defocus value, each wall’s position separately.

Figure 41 Combined interlayer spacings of the thin graphite particle. The index 1-2-3 denotes the mean value of the outermost and the second outermost spacing: 1-2 and 2-3.

Figure 40 shows many single data points and relatively high fluctuations. Their average values vary less from each other, within 0.34 nm and 0.36 nm. It can be seen that at underfocus the outermost spacings (index 1-2 and 6-7) show values smaller than the average values.

It should also be noted that some single spacings appeared to have extraordinary values (for example spacing 1-2 at defocus -50 nm in Figure 40). Similar extremes can be seen as well in Figure 44 and Figure 46. These extremes have their origin probably in the change of the wall’s appearance due to the defocus. At some defocuses, some walls happen to be extraordinarily dark. This is likely due to diffraction effects and is shortly shown in Figure 67 in the appendix.

For a simplified presentation, in Figure 41 the 6 spacings of this graphite particle are combined to three pairs, the two outermost (1-2-3), the two in the middle (3-4-5), and the two innermost (5-6-7) walls. Considering what we ultimately want to research - a different spacing
of innermost compared to outermost layers - this paired combination should still show such a circumstance.

So far for graphite, it can be identified that in underfocused images the outermost spacings (at both ends of the particle) have relatively smaller values. This probably happens by an influence of the bright Fresnel fringe.

The measured average values vary in a range from about 0.340 nm to 0.370 nm and it looks like the spacing values are most consistent at around the Scherzer defocus (about -50 to -100 nm in Figure 37 and about 0 nm in Figure 39).

**Impact on CNTs’ spacings**

**Figure 39** shows sections of TEM images of nanotubes being researched in this chapter. First, the outer- and innermost walls are not taken into account and just the middle spacings are determined (**Figure 43**). Finally, of Tube 1 and Tube 2 all walls and their individual positions are taken into account (**Figure 44-Figure 47**).

**Figure 42** The analyzed sections of a) Tube 1; b) Tube 2; c) Tube 4.

**Figure 43** Defocus dependence on average spacings (4 spacings) of the middle walls (outer- and innermosts excluded) of Tube 1, Tube 2 and Tube 4 (for Tube 4 it’s the average of 6 spacings).
Those middle walls’ averages values fluctuate between 0.350 and 0.380 nm with a standard deviation of about ±6 % (±0.02 nm). The iron-filled CNT’s spacings have smaller standard deviations. At a moderate defocus around 0 nm, the trends are similar to each other with a spacing of about 0.36 nm.

The next step is to consider both all walls and their positions separately – or paired. The values of Tube 1 are shown in Figure 44 and Figure 45.

**Figure 44** Interwall spacings of Tube 1, dependent on the defocus value, each wall’s position separately.

**Figure 45** Combined interwall spacings of Tube 1 dependent on defocus. The index 1-2-3 denotes the mean value of the outermost and the second outermost spacings: 1-2 and 2-3.
The interwall spacings, separately and paired, of Tube 2 are shown in Figure 46 and Figure 47.

![Figure 46](image1.png)

**Figure 46** Interwall spacings of Tube 2, dependent on defocus and each wall’s position separately, dependent on defocus.

![Figure 47](image2.png)

**Figure 47** Combined interwall spacings of Tube 2. The index 1-2-3 denotes the mean value of the two outermost spacings: 1-2 and 2-3.

Both Figure 44 and Figure 46 shows similar average values of about 0.360 nm, with their smallest error bars at a slight underfocus (defocus -20 nm and 0 nm). In addition, the tubes’ inner- and outermost spacings are smaller in underfocused images. Furthermore, it can be recognized that the innermost spacing (index 6-7, seen in both CNTs and similar in the researched thin graphite particle) shows the biggest variations, being almost up to 30% variant from the average.
So far for CNTs, considering the measuring accuracy, a clear dependency of the general measured spacings on the defocus value can’t be identified, but it can be seen that the spacings’ variation is smallest for a slight underfocus (about -20 nm).

Summarizing, it can be concluded that the measured single spacings show relatively large fluctuations between different defocuses. The calculated average values however, show moderate and expected values. Therefore, we conclude the measured interwall and interlayer spacings of graphite particles and CNTs are in general not dependent on the defocus. Except this, it should be expected that in underfocused images the spacing values of the inner- and outermost walls / layers are smaller than the other ones. Additionally, the measured spacings’ variations are relatively the smallest at a slight underfocus, between zero and Scherzer defocus.
5. Discussion

Our results compared to the previous studies

It is possible to see already in **Figure 44-Figure 47** that, for example, the innermost interwall spacings are not always larger than the outermost ones. In the following, for an improved comparison with the previous studies, three different possible trends of the interwall spacing - dependent on the tube’s outer diameter (**Figure 48**), the individual wall’s diameter (**Figure 49**) and the wall index (**Figure 50**) - are shown.

In addition to the interwall spacings, now the tube’s inner and outer diameter is determined as well. Those are only rough values as our researched CVD grown CNTs don’t show a perfectly constant diameter. For the following short comparisons, a diameter’s accuracy of ±0.5 nm is acceptable.

**Annotation:**
In **Figure 48, Figure 49** and **Figure 50**, our measured spacings are corrected by 3 % which is compensating the instrument’s imaging excess shown by the gold calibration.

**Figure 48** The interwall spacings of Tube 1, Tube 2, Tube 3 and two of the researched tubes in the paper from (Kiang et al. 1998), dependent on the tube’s outer diameter. In each data point either 5 or 6 spacings are averaged. The dashed lines indicate the empirical equation from (Singh et al. 2010) and a constant value of 0.344 nm.
Figure 49 The interwall spacings of Tube 1, Tube 2, Tube 3 and two of the researched tubes in the paper from (Kiang et al. 1998): “Small Tube” and “Medium Tube” and the spacing values for the 5- and 10-walled MWCNTs from (Huang et al. 2010), dependent on the individual walls’ position, denoted with a spacing index. In each data point of Tube 1, Tube 2 and Tube 3, either 2 or 3 spacings from different defocuses are averaged (error bars are not shown because of the density of information). The spacing index 9-10 denotes the innermost spacing, 1-2 denotes the outermost one.

Figure 50 The interwall spacings of Tube 1, Tube 2 and Tube 3, dependent on the individual wall’s diameter. In each data point either 2 or 3 spacings (from different defocuses) are averaged and define the shown error bars. The dashed lines indicate the empirical equation (Kiang et al. 1998) and the spacing values for the 10-walled MWCNT (Huang et al. 2010), converted by us to base on the individual wall’s diameter.
We see in Figure 48 that our results are not really in concordance with the conclusions from (Singh et al. 2010). The obtained spacing values from our research and the spacing values of two tubes out from (Kiang et al. 1998) are clearly smaller than the suggested empirical fit and don’t show the suggested trend.

As seen in Figure 49, our obtained values show a very similar trend like the expected one out of the calculated interwall spacings although our values are on average slightly higher. Interestingly, the middle layers’ spacings of the researched Tubes 1-3 are in agreement with the calculated ones.

In Figure 50, a slight spacing’s trend could be guessed, even similar to the expected one from (Kiang et al. 1998). On the other hand, considering the previously described inaccuracy of up to 10 % by taking a single information out of a TEM image, we will be careful in formulating a conclusion as the trend is relatively slight and the error bars are calculated from only 2 and 3 measurements. This research needed to be continued with analyzing several MWCNTs, especially smaller ones.

6. Final Conclusion and Outlook

Through our experiences of examining some defocus series, we propose an imaging procedure of taking 10 images of the same nanotube within the range of being blurred because of underfocus and being blurred because of overfocus. With the help of those 10 images, one should be able to recognize any ‘wrong’ information that might occur due to Fresnel fringes.

In order to analyze the CNT interwall spacings out of TEM images we examined several error sources. As all of them are smaller than 10 %, we claim this percentage as an expected inaccuracy and we determine it is sufficient to put the sections of the contrast profiles (carefully) by naked eye.

We couldn’t identify any clear trend of the general measured distances dependent on the images’ defocus value, although single spacings can vary a lot between different defocuses. It can be noted that the measured spacings’ variations are relatively the smallest at a slight underfocus, between zero and Scherzer defocus.

With our analyses, we can suppose that the interwall spacings are not as strongly varying as the previous study (Singh et al. 2010) concludes, but our analyses are relatively in harmony with the two other studies from (Huang et al. 2010) and (Kiang et al. 1998). The interwall spacings from tubes with an inner diameter larger than 5 nm are relatively constant within the whole tube. We can’t make a statement about the spacings’ increase for tubes with a smaller inner diameter - from (Kiang et al. 1998) - as we didn’t research tubes with this size. It appears that the middle spacings (excluding the outer- and innermost ones) show values that are most consistent with the interlayer spacings of turbostratic graphite. In underfocused images, the outer- and innermost spacings tend to have spacings being slightly smaller than the middle ones from the same tube.

In general, it is evident that a clear conclusion by considering only three tubes (or five by adding the two tubes from the study (Kiang et al. 1998)) is not possible. At the beginning of writing this work, the plan was to research plenty of carbon nanotubes and obtain statistically trends with the data. But as it turned out, most of the time was spent in obtaining cognitions for what needs to be considered in taking and researching TEM images of carbon nanotubes.
With the help of those cognitions, it is the task of future research to extend the measured data and improve our conclusions about the spacings’ dependence on the tube size.

### 6.1 Image treatment

It might happen that the most interesting part of TEM images are blurred due to being defocused and it is very difficult to interpret all the information from a single image. If so, there are possibilities to improve images with noise due to defocus by treating them with a software using a so-called exit wave reconstruction. A possible image’s improvement for example with the Software *Truelmage* is shown in **Figure 51**. (Kübel & Thust 2005)

**Figure 51** a) Underfocused HRTEM image of twin boundaries in BaTiO3. The arrow indicates the contrast delocalization; b) Improved image, treated with the exit wave function (phase) and after correction of residual aberrations and coma.

### 6.2 Other CNT material

Within this work, only CVD grown carbon nanotubes were analyzed. We haven’t checked if those cognitions are the same for other CNT material. One could for example imagine that annealed CVD grown tubes have a slightly smaller interwall spacing due to the extinguishing of defects. Furthermore, in general, arc discharge grown tubes have a more perfect structure that could have an effect on the interwall spacings as well.

**Figure 52** TEM image of a CNT grown by the arc discharge method.
7. References


Internet source 2, http://www.frontiersin.org/files/Articles/89051/fnsys-08-00091-HTML/image_m/fnsys-08-00091-g002.jpg.


8. Appendix

8.1 TEM images of the researched CNTs

The researched TEM images of CNTs have been made with an acceleration voltage of 90 kV and at a magnification of 600k.

Figure 53 TEM image of Tube 1.  
Figure 54 TEM image of Tube 2.

Figure 55 TEM image of Tube 3.  
Figure 56 TEM image of Tube 4.

Figure 57 TEM images of Tube 3; a) defocus -60 nm, correlating with Figure 27; b) TEM image of Tube 3, defocus -30 nm, correlating with Figure 28.
8.2 TEM’s calibration and accuracy

For checking the instrument’s accuracy, we analyzed a gold sample in our TEM. The visible patterns (seen in Figure 26) are mostly belonging to the (111)-spacing of gold (0.2354 nm). Figure 58 shows those inter-planar spacings at different defocuses and from different particles and two different magnifications. Each of those data points is the average of 6 measured adjacent spacings.

![Graphs showing inter-planar spacings](image)

**Figure 58** The graphs show the inter-planar spacing dependent on the TEM’s defocus value. Each graph is correlating to another particle. The graphs a and c were made with an image at x400k mag, b and d at x600k mag. Graph d shows additional another gold plain spacing (200) to confirm that the smaller values of this particle are not due to another researched plain.

In the analysis first an excess of some percent can be seen, but the results in _33f actually are pretty consistent with the real layer distance of gold. Due to the almost perfect fit one could imagine that there is a connection between the measured values and the regarded matter’s orientation. This was checked by measuring the (111)-spacing of a selection with horizontal and vertical spacing-lines. The results are shown in **Figure 59**. In the graphs a, c and d we have three surely different orientations and all of them show the similar excess. Therefore, any matter’s orientation dependence can’t be affirmed.
Figure 59 Inter-planar spacings dependent on the TEM’s defocus value, correlating with different gold particles (from the same TEM image); a) the particle’s orientation of is very similar to the one of Figure 58d; b) is just a random other particle from the same image; c) this graph correlates with a particle having horizontal planes; d) this graph correlates with a particle having vertical planes.

The particle’s planes orientations of Figure 58d and Figure 59a are almost the same. But Figure 59a shows a slightly excess like all the other graphs, except Figure 58d (which let us conclude that this perfect fit happened just at random).

All in all, we can affirm there is an excess of about 3.0 % (exactly 2.98 %, average out of 6 analyses).
8.3 Influence of a tilt and the width of the chosen section for the contrast profile

As the chosen sections for the contrast profile are created and positioned by naked eye, it could be that they have a tilt which might cause the section’s fringe not being in a perfect line with the inspected walls or planes. This is researched in Figure 60–Figure 64.

![Figure 60 TEM images of Tube 4 showing the sections for the contrast profiles; a) a not tilted section (defined by us); b) the section at a tilt of 4 degrees. For a better comparison, the dashed shape shows again the not tilted section. The two images (mag x600k) show a part of an iron filled CNT at a defocus value -20 nm.](image)

![Figure 61 Average values interwall spacing, dependent on tilt of the profile section, correlating with Figure 60.](image)

We see from Figure 61, a tilt of two degrees changes the average value only by 1.4 %, the error value is about the same. A tilt of four degrees neither changes the average value much, but the error value gets about tripled (4%).

In the next step, the section’s tilt for another case is researched, considering now as well the dependence of the section’s width.
Figure 62 TEM images (mag x600k) of a graphite particle showing the sections for the contrast profiles. The section’s width is 100 px (2.3 nm); a) a not tilted section (defined by us); b) the investigated section at a tilt of 4 degrees, for a better comparison, the dashed shape shows again the not tilted section.

Figure 63 TEM images (mag x600k) of a graphite particle showing the sections for the contrast profiles. The section’s width is 25 px (0.6 nm); a) a not tilted section (defined by us); b) the investigated section at a tilt of 4 degrees, for a better comparison, the dashed shape shows again the not tilted section.

Figure 64 The two obtained trends for the profile section’s dependence on its tilt and its width.
Due to a slightly exceeded value for the outermost spacing, those are excluded of the analysis. In Figure 64, an average value out of 5 measured spacings is considered. It can be seen, between the two widths there is an average’s difference of about 0,005 nm (1.4 %) identifiable. Within one width, the average values changes very slightly by about 0.005 nm (1.4 %) as well. On the other hand, the average values itself have a standard variation of about 3 % (2.8 % at width 100 and 3.7 % at width 25).

The slightly larger deviation in the width25’s trend is in harmony with theoretical expectations which shows that a wider integration section is more affected by a section’s tilt compared to a narrower section. (This happens due to an integration’s line crossing with more than one layer / wall in the tem image).

The results regarding Figure 64 look even better than the results shown in Figure 61. By comparing the average values and the relative errors (the standard deviation) of all three analyses they are pretty similar. The averages are between 0.365 and 0.370 nm with a general variation for one interlayer-spacing-value of about 3%. The contrast profiles with a wider integration section show in general a smoother current, but according to our results, with our procedure the less smooth current doesn’t affect the results in a relevant way.

Summarizing, we determine that in a tilt’s range of 0 to 4 degrees, there is no identifiable change due to the integration section’s width (width up to 2.3 nm) or its tilt. And a tilt less than 4 or even less than 2 degrees is feasible by naked eye.
8.4 Comparison contrast profiles of different defocuses

Figure 65 shows the appearance of a ghost wall in smaller defocus steps. We tried to follow the trend of single peaks and dips which are causing each profile. The black lines are referring to the dip-dip distance (they allow to show the approximate interwall spacing even outside the real CNT), the blue and the orange curves describe dips and peaks, respectively.

Figure 65 Contrast profiles of Tube 2 at 5 different defocuses.
8.5 Comparison of the defocus series images of two researched CNTs

Figure 66 and Figure 67 show a comparison of the TEM images from Tube 1 and Tube 2 obtained from the defocus series. The purpose of this comparison is to show the images’ trend at different defocuses and the appearance of additional walls. The images are supposed to be positioned in a way that the same walls should touch each other between different defocuses. We do this positioning while considering a detailed comparison of the contrast profile, but in some situations – especially in highly underfocused images – this positioning is slightly doubtful and therefore it can’t be trusted a hundred percent.

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Figure 66 Comparison of the images of Tube 1 at different defocuses.
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Figure 67 Comparison of the images of Tube 2 at different defocuses. In the images at defocus -60 and -40 nm, two sections are dashed. These sections refer to chapter 4.2.2 and show some walls being extraordinarily dark which causes some extraordinary spacing measurements. These dark spots / areas are not showing real information about those specific walls. As they are different from defocus to defocus, they are probably caused by diffraction effects.