Kinetics of Carbon Nanotube scission under Sonication
a Consecutive first-order reaction with a length-dependent scission rate.

Joris Stegen
Supervisor: prof. dr. ir. P.P.A.M. van der Schoot

Eindhoven University of Technology - Theory of polymers and soft matter

May 27, 2011
Abstract

A dispersion of individualised carbon nanotubes is commonly obtained by means of sonication. Under sonication bundles of nanotubes are debundled, a process known as exfoliation. During sonication small bubbles within a liquid are brought into oscillation by an acoustic field. Under certain conditions these oscillations can end in the violent collapse of the bubble. This disruptive process disperses the nanotubes and is known as transient cavitation. From experiments it is well known that this process is also responsible for the scission of individual nanotubes. The scission of carbon nanotubes under sonication is investigated in this report. A mechanical model for scission based on the interaction between a single bubble and nanotube is constructed. The model indicates that scission will occur at the middle of the nanotube as long as it is sufficiently long. Furthermore it is shown how a length-dependent scission rate can be derived and how the presence of defects can slow down the scission process. The scission process is modeled as a series of consecutive first-order ‘reactions’. A mathematical description of the length distribution is obtained and the possibility of scale invariance in the length distribution is investigated. Finally both the mechanical model and the mathematical description of a consecutive process are combined to obtain a mathematical description of the scission process. This description is compared to simulation results and it is shown that theory and simulation are mostly in agreement.
1 Introduction

The subject of this report is the “scission of nanotubes under sonication”. This is a fascinating subject for a simple reason: a carbon nanotube is the strongest material known to mankind in terms of tensile strength and yet the subject of this report suggests that a simple, small, oscillating bubble can cause the scission of it! Either there is a very clever and intriguing mechanism at play which allows for the scission of the nanotube, or the small oscillating bubbles are not as harmless and simple as one would perhaps naively assume.

From a technical point of view, the problem is very relevant as well. The quality of a polymeric bulk material can be enhanced by dispersing a small amount of individualised carbon nanotubes in it. This is not so easy, carbon nanotubes tend to self-organise into ropes and bundles. Usually the ropes and bundles are broken up into individual nanotubes by means of sonication. From experiments it is well known that sonication will not only exfoliate the nanotube ropes but will also cause the scission of individual nanotubes. As the properties of a nanotube strongly depend on its length, it is very relevant to understand this scission process. The aim of our work is to understand how the length distribution of nanotubes will evolve during sonication. To this end a theoretical model is constructed in this report.

Important in the construction of this theoretical model for nanotube scission is the experimental work done by Poulin et al. [1] in Bordeaux. In figure 1 a plot of their results is shown. This plot gives two important clues on the scission dynamics. Firstly, the average length decreases linearly in a double logarithmic plot, indicating that the average length should be a power-law function of the supplied energy. Secondly, this power-law decay suggests that the length distribution of nanotubes could potentially display dynamical scale invariance. In our attempt to model the dynamics of nanotube scission, we aim to reproduce both observations.

Figure 1: On the left a schematic representation of the consecutive breaking of a single nanotube. At a certain moment the nanotube breaks into two segments of equal length. At a later moment one of these segments has again broken into two and at an even later moment some segments have broken again. On the right the average nanotube length as a function of the supplied acoustic energy is shown in a double logarithmic plot [1].

A carbon nanotube is a nanoparticle with many unique properties. In shape it resembles a long and thin needle. The diameter of a nanotube is of the order of 1 nm up to 50 nm while the length of the nanotube can be of the order of a centimeter though typically the nanotube length is of the order of a micron or less. Aside from its high tensile strength, a carbon nan-
otube has excellent thermal and electric conductivity. When a small amount of nanotubes is dispersed in a material, some of these remarkable properties can be bestowed upon the bulk material. For example, the electric conductivity and stress transfer of the bulk material can be improved when nanotubes form a percolating network through the bulk material. The percolation threshold strongly depends on the nanotube length and decreases with increasing nanotube length [2]. From this point of view, it is useful to have long nanotubes.

One of the less desirable properties of nanotubes is their toxicity. Numerous studies have shown that carbon nanotubes of at least 20 µm, which are similar in shape to asbestos, will cause damage to living tissue [3]. Especially our lungs are sensitive to the effects of inhalation of carbon nanotubes, if exposed for a prolonged time the risk of lung cancer becomes very real. It would be desirable to use carbon nanotubes with a maximum length of 20 µm.

Carbon nanotubes are strongly hydrophobic, as a result the nanotubes tend to self-organise into so-called ropes or bundles in an aqueous solution. When carbon nanotubes are produced, they are produced as bundles of carbon nanotubes. In order to obtain a dispersion of individualized nanotubes, the nanotubes are sonicated and stabilized by the addition of surfactant. During the sonication process, scission of individual nanotubes will also occur. The length distribution of the nanotubes in the dispersion is altered and the average length of the nanotubes in the dispersion changes. Whether a nanotube will be broken, depends on its tensile strength. In chapter 2 the mechanical properties, including the tensile strength, of carbon nanotubes are briefly discussed.

The process of sonication is due to the presence of small, oscillating bubbles within the liquid. In a sonication process an ultrasound acoustic field is applied to a liquid. This acoustic field induces the oscillation of the small bubbles. The disruptive properties of these bubbles are then, for example, used in the sonication process to disperse small particles throughout the liquid or thoroughly clean surgical tools. That small bubbles within a liquid are not as harmless as they appear to be has actually been known for some time now. It was Lord Rayleigh who first studied the dynamics of a bubble in water, after he had been consulted by hydraulic engineers in 1917.

These engineers were worried about the erosive effects that small bubbles can have on hydraulic components such as a ship propeller. A second hint to the rather violent nature of these oscillating bubbles is the effect of sonoluminescence. In 1934 this effect was discovered at the University of Cologne. Scientists had attempted to speed up the development process of a photograph by introducing an ultrasound field to the tank of photographic developer fluid. Their experiment resulted in numerous tiny dots on the film they developed! The small oscillating bubbles had emitted light during the development of the film. Later on, spectral analysis revealed that the light emitted corresponds to temperatures of up to 5000 K within the bubble [4]. Responsible for these processes is the violent implosion of bubbles within the liquid, a process known as transient cavitation.

In chapter 3 the process of transient cavitation is discussed and the collapse of a bubble is modeled with Lord Rayleigh’s model for the collapse of an empty cavity. In chapter 4 the transient collapse of a bubble is approximated by this model. Unfortunately, it will be shown that by modeling the transient collapse of a bubble with Rayleigh’s model, we cannot explain the scission of nanotubes.
In our model the interaction between a single nanotube and a single bubble is investigated. Interactions between multiple bubbles and or nanotubes are neglected. In chapter 4 the mechanics involved in the scission of the nanotube are discussed. It is shown that scission will occur right at the middle of the nanotube. A minimum length for which scission will still occur and a length-dependent scission rate is derived. Finally it is shown that the presence of defects, which locally lower the tensile strength of a nanotube, can slow down the scission process.

The scission process is a consecutive process, a long nanotube can break into two pieces of equal length, each of these pieces can break again and so on. This consecutive breaking is shown on the left in figure 1. In chapter 5 the mathematics of such a consecutive first-order process are discussed. The mathematics are based on a set of differential equations, which describe how the occupation of the states in the consecutive process evolves in time. An exact solution for a process with a constant reaction rate as well as a solution for a system with non-constant reaction rates is given. It is shown that the distribution over the consecutive states is approximately gaussian for sufficiently large times. In the final paragraph of this chapter it is assumed that the length distribution is of a specific mathematic form and a power law for the average length is derived.

Finally, in chapter 6 the scission process is simulated with a Monte Carlo simulation. In these simulations the scission of a nanotube occurs right at the middle of the nanotube until the minimum length for scission is obtained. The mathematics as derived in chapter 5 are compared to the results of the simulations and it is shown that theory and simulation are in agreement.

In chapter 7 it is discussed how dispersions of carbon nanotubes can be used in touch screen technology. Currently thin layers of Indium tin oxide are being used, but this is an expensive material. An alternative, which might turn out to be cheaper, is a thin layer of a carbon nanotubes. To produce such a layer, a dispersion of individualised nanotubes must be obtained by sonication and deposited onto the surface. With the abundance of touch screen technology in mobile devices, the topic of carbon nanotube scission is clearly relevant to industry.

In the last chapter, the summary and outlook, the important results are summarised and the parts of this report which require additional work are listed.
2 Carbon Nanotubes

A carbon nanotube could be described as a one-dimensional diamond. Though carbon nanotubes do have remarkable properties, the comparison is not really valid. In a diamond each of the four valence electrons of the carbon atom form an \( sp^3 \) bond with a valence electron of another carbon atom. The carbon atoms in a nanotube form a bond with just three neighbouring carbon atoms, three of the four valence electrons are in an \( sp^2 \) state while the fourth electron is in a \( \pi \) state. This makes a comparison to graphite or graphene more valid. Especially the comparison to graphene is very good, a carbon nanotube should be pictured as a single sheet of graphene rolled into a long narrow tube. Both a carbon nanotube and sheet of graphene or shown in figure 2.

![Image](image.png)

Figure 2: On the left a schematic picture of a sheet of graphene is shown [5]. On the right a schematic picture of a carbon nanotube is shown [6].

In this chapter the different sorts of nanotubes are briefly discussed, relying rather strongly on the book “Carbon Nanotubes: Science and Applications” by M. Meyyappan [7]. Nanotubes that exist of just a single sheet of graphene are the so-called single-wall nanotubes. Multi-wall nanotubes also exist and they should be pictured as a sheet of graphite of just a few atomic layers rolled into a long and narrow tube.

2.1 The chiral vector

There are many ways to make a nanotube out of a sheet of graphene. How the nanotube is made of the sheet is described by the chiral vector of the nanotube. To understand what this vector is and how it defines the structure of the nanotube it is best to do a small experiment with a sheet of paper. Just take the sheet of paper and make a tube of it. Most likely you will now have two corners on top of each other at each side of the paper tube! You can decrease the tube radius by rolling it into a tighter paper tube. Notice how each corner is now on top of a different piece of paper. You can also introduce an offset between the two corners of the sheet of paper, the seam will now twist around the paper tube.

By stating which two points should be layed on top of each other you can define the structure of the tube. Not so surprisingly, this is exactly what the chiral vector does. It points from any given lattice point on the graphene lattice to the lattice point to which it should be connected to construct the nanotube. The chiral vector, \( C \), is expressed in the two lattice vectors of the sheet of graphene:

\[
C = (n, m) = n\vec{a}_1 + m\vec{a}_2. \tag{1}
\]
In figure 3 three different nanotubes are constructed from a sheet of graphene, the corresponding chiral vectors are drawn on the graphene. The properties of a nanotube strongly depend on the chiral vector of the nanotube. For example, depending on its chiral vector a single-wall nanotube can be metallic or semiconducting. The dependence of nanotube properties on the exact value of the chiral vector is however outside the scope of this report.

2.2 Mechanical properties

The strength of a particle is described by its tensile strength, \( \sigma_b \), and its Young modulus. The tensile strength is the maximum force a particle can withstand per unit surface without breaking. The Young modulus measures the stiffness and gives the required force per unit surface to stretch the material up to twice its initial length. For a carbon nanotube the surface is equal its cross section: \( \pi d^2 / 4 \) where \( d \) is the nanotube diameter. A single-wall nanotube typically has a radius of 0.6 nm up to 2 nm. The theoretical tensile strength of a single-wall nanotube is of the order \( \sigma_b = 75 \text{ GPa} \). The Young’s modulus is of the order of 1000 GPa.

For a multi-wall nanotube the diameter is typically of the order of 10 to 100 nm. The extra layers of graphene in a multi-wall tube add to its tensile strength, for a multi-wall nanotube the tensile strength is of the order of \( \sigma_b = 150 \text{ GPa} \) while the Young modulus is of the order of 1200 GPa. To put this in perspective, a weight of 15,000 kg could be supported by a nanotube with a 1 mm\(^2\) cross section and a tensile strength of 150 GPa, while a weight of just 86 kg can be supported by a wire of stainless steel with an identical cross section [8].

An important assumption in the model constructed in this report, is that the nanotubes will behave as a rigid rod-like particle. This assumption is reasonable as long as the length of the nanotubes is of the order of the persistence length or shorter. For a single-wall nanotube a persistence length between 32 \( \mu \text{m} \) and 174 \( \mu \text{m} \) is reported [9], so this seems a reasonable assumption as nanotubes typically have a length of about a micron.

As mentioned in the introduction, carbon nanotubes are produced as clusters of nanotubes known as ropes or bundles. In a rope the nanotubes form a triangular lattice in which the tubes are held together by van der Waals forces. Multi-wall nanotubes are still hydrophobic but do not organise into ropes or bundles. Remember that the hydrophobic nature of the nanotube is the very reason why they need to be sonicated to obtain a dispersion. As it is somewhat easier to obtain a dispersion of individualised multi-wall nanotubes, the scission
of multi-wall nanotubes will be considered in this report. It will be easier to compare the results of the model to actual experimental results on the scission of carbon nanotubes under sonication as obtained by Poulin et al. [1]. These experimental results were obtained by sonicating a dispersion of individualised nanotubes. As a preparation for the actual experiment, the nanotube bundles are exfoliated by sonication and stabilised by the addition of a surfactant. Though the effects of clustering and bundling are not considered in our model, the model should also be applicable to single-wall nanotubes. A second effect, that occurs for single-wall nanotubes that is not included in our model is, that two single-wall nanotubes can rejoin to form a single nanotube again, the scission process is reversible.

2.3 Defects

A nanotube is an ordered, crystalline material and just like any other crystalline material it will contain defects. Many types of defects exist, think of vacancies, structural defects which result in a bend or branching. A small bud (like a bucky ball) can grow on the nanotube or the nanotubes can be capped by half a bucky ball. Bamboo-like nanotubes have been observed in which multiple capped segments are joined together, see figure 4.

![Figure 4: A defective multi-wall carbon nanotube with a bamboo like structure.][7]

The possible types of defect are not discussed in any detail in this report. Two important remarks regarding the defects should be made though. First, the type and number of defects present in a nanotube will depend on the production method. Second, and perhaps more importantly, the presence of defects will locally lower the tensile strength of the nanotubes. In the previous paragraph a tensile strength of $\sigma_b = 150$ GPa for multi-wall nanotubes was given, yet experimental measurement of the tensile strength give a value of approximately $\sigma_b = 2$ GPa [10]. The article concludes that this deviation from theory is not necessarily the result of defects within the nanotube though. In paragraph 4.4 the effect of defects on the scission dynamics is discussed.

In our calculations throughout this report a nanotube with a diameter of 10 nm and a tensile strength of $\sigma_b = 10$ GPa will be used, although the results of our work can be generalised for a nanotube of arbitrary dimensions and tensile strength.
3 Bubble dynamics & Sonication

How does a small bubble break one of the strongest materials that is known to mankind? The answer is in principle simple: the bubble must somehow exert a force on the carbon nanotube large enough to overcome its breaking strength. The question is, how can a bubble exert such a large force? The process that is responsible for the scission is well studied, but not fully understood.

Sonication is a widely used technique, which relies on this process. For example, surgical instruments are cleaned by sonication. The technique is also used to evenly disperse nano-particles, such as carbon nanotubes, in a liquid medium. It is during this process that the scission of carbon nanotubes occurs. In the literature, it is generally assumed that the process of transient cavitation, the violent implosion of a bubble, is responsible for the scission of the carbon nanotube.

Assuming that this is indeed the case, there are two important questions:

- How large is the force that an imploding bubble exerts on a carbon nanotube in the liquid?
- What determines the number of imploding bubbles that are generated per unit time and unit volume?

Both questions can be answered on the basis of experimental results.

- In a study by Poulin et al. [1], experiments on carbon fibers with known mechanical properties show that the radial flow around an imploding bubble generates a strain rate of up to $6 \times 10^9$ s$^{-1}$. A simple mechanical model indicates that such a strain rate is sufficient to break carbon nanotubes. This model is discussed in chapter 4.

- The same study also provides an answer on the second question. The experiments reveal that the decrease in average length depends solely on the amount of acoustic energy supplied to the system. This suggests that the number of imploding bubbles is proportional to the acoustic power supplied to the system.

In a sonication experiment a high frequency acoustic field is applied to a liquid medium. As a result of the acoustic field, small bubbles are nucleated within the liquid, which are then brought into oscillation by the acoustic field. These oscillations can become unstable and end with the violent implosion of the bubble.

The nucleation of bubbles within the liquid and the different oscillation types of these bubbles are discussed in the next paragraphs. In the discussion we will try to find a theoretical basis for the answer to the two questions as given above; in this discussion the parameters of the experiments performed by Poulin et al. will be used in calculations on the process of transient cavitation. This chapter was written with extensive use of the book “The Acoustic Bubble” by T.G. Leighton [11] and a series of articles on acoustic cavitation [12, 13, 14, 15, 16].

3.1 The acoustic field

In the sonication process a harmonic acoustic field with a certain frequency and power is applied to the liquid in the sonication bath. The threshold for both bubble formation and
transient cavitation depend on the amplitude of the acoustic oscillation. This amplitude is defined as the acoustic pressure, $p_A$. Note that the applied acoustic pressure is negative for half the period of the harmonic oscillation. In magnitude the negative pressure can be greater than the static ambient pressure, resulting in a temporary negative liquid pressure.

The acoustic power, $P_A$, is defined as the product of the sound intensity, $I$, and the area, $A$, through which the sound wave passes, $P_A = I \cdot A$. The sound intensity is defined as the mean square acoustic pressure divided by the specific acoustic impedance, $Z$,

$$I = \frac{P_A^2}{Z}. \quad (2)$$

Finally, the acoustic impedance, $Z$, is defined as the product of the mass density, $\rho$, and the speed of sound, $c$, within the material, $Z = \rho c$. It is a measure of the reaction of a material to an applied acoustic pressure. The acoustic pressure is then given by:

$$p_A = \sqrt{\frac{P_A Z}{A}}. \quad (3)$$

For a sonication power of $P_A = 10$ W and a horn surface of 1 cm$^2$ the root mean square acoustic pressure within water at room temperature is then of the order of $p_A = 4$ bar. This is an approximation of the acoustic pressure right at the surface of the sonicator horn. Within the sonication bath the acoustic pressure will be lower, the acoustic energy is spread over a larger surface and there will be losses in acoustic pressure due to attenuation. Furthermore, it should be noted that the presence of bubbles within the liquid will have an effect on the acoustic field.

The important conclusion from the above is that, to be able to reach a pressure threshold twice as high, the acoustic power must be increased by a factor of 4. The acoustic power is proportional to the square of the acoustic pressure.

### 3.2 Acoustic Cavitation inception

Acoustic cavitation was defined by Apfel as “Any observable activity involving a bubble or population of bubbles stimulated into motion by an acoustic field” [15]. This implies that there are either some pre-existing bubbles within the liquid medium or that the bubbles are created by the acoustic field. The idea of pre-existing bubbles is problematic. As a result of their buoyancy, any bubble with a radius of the order of 1 $\mu$m or larger will simply float toward the surface and disappear from the liquid.

Though the movement of smaller bubbles is dominated by Brownian motion rather than gravitational effects, small bubbles will also disappear as they dissolve into the liquid. The dissolving of the bubble is the result of diffusion of gas out of the bubble. This diffusion is due to a gradient in the concentration of dissolved gas in the liquid close to the bubble and liquid far from the bubble. Both mechanisms through which bubbles are removed from a liquid are shown in figure 5. The dissolution of small bubbles is discussed in more detail in the rest of this paragraph.

Henry’s law states that in equilibrium the concentration of a gas which is dissolved in a liquid is proportional to the partial pressure of that gas within the body of gas with which the liquid is in contact. For a sonication experiment this would mean that the concentration
of a given gas which is dissolved in the liquid is proportional to the partial pressure of this gas in the air above the sonication bath.

\[
\frac{R}{M_m} > 1 \Rightarrow \text{Buoyancy}
\]

\[
\frac{R}{M_m} < 1 \Rightarrow \text{Dissolution}
\]

Figure 5: The bubble on the left has a radius \( R > 1 \, \mu\text{m} \), as a result of buoyancy it will float towards the surface and be removed from the liquid. The bubble on the right has a radius \( R < 1 \, \mu\text{m} \), it will dissolve into the liquid due to a concentration gradient in the amount of dissolved gas between the liquid near the bubble and far from the bubble.

Now consider a small bubble within the liquid. According to Henry’s law the concentration of dissolved gas in the liquid just beyond the surface of the bubble should be proportional to the partial pressure of this gas within the bubble. Below it is shown that due to the effects of surface tension, \( \sigma \), the partial gas pressure within a bubble, \( p_{g,b} \), will be greater than the partial pressure of the same gas in the air above the sonication bath, \( p_{g,a} \).

Surface tension is defined as the free energy per unit of surface and it is a measure of the cost of creating an interface, for water at ambient conditions the surface tension is approximately equal to \( 72 \cdot 10^{-3} \, \text{Nm}^{-1} \) [17]. For a spherical bubble the surface tension tries to decrease the bubble radius and as a result minimise the surface of the interface between the bubble and liquid. The surface tension is balanced by an excess pressure in the bubble which is known as the Laplace pressure, \( p_\sigma \). If the bubble has a radius \( R \), the Laplace pressure is given by:

\[
p_\sigma = \frac{2\sigma}{R}.
\]  

(4)

In equilibrium the internal bubble pressure, \( p_i \), must be equal to the external liquid pressure, \( p_l \), plus the Laplace pressure, \( p_\sigma \), as is shown in figure 5. If the interaction between vapour and gas is neglected, the internal pressure of the bubble is equal to the sum of the gas pressure in the bubble and \( p_{v,b} \), the vapour pressure in the bubble:

\[
p_i = p_{g,b} + p_{v,b} = p_l + p_\sigma.
\]  

(5)

For a sufficiently shallow sonication bath in ambient conditions, the hydrostatic pressure can be neglected and the liquid pressure is approximately equal to the atmospheric pressure \( p_l \approx p_0 \). The vapour pressure in the bubble can be considered as constant; the transfer of solvent molecules into or out of the bubble is very fast. The excess pressure within the bubble, the Laplace pressure, must then be generated by the gas present within the bubble. As a result the partial gas pressure in the bubble must be higher than the partial pressure of the corresponding gas in the air above the sonication bath, \( p_{g,b} > p_{g,a} \).

According to Henry’s law, this difference in partial gas pressure results in a gradient in the concentration of gas dissolved in the liquid close to the bubble and the amount of gas dissolved in the liquid far from the bubble. This concentration gradient results in a gradient in the chemical potential, which in turn results in the diffusion of dissolved gas away from the
bubble. The gas that has diffused away from the bubble is in turn replaced by some gas that diffuses out of the bubble into the surrounding liquid, as a result the bubble shrinks. As the effects of surface tension increase with decreasing bubble size (equation (4)), the difference in concentration of dissolved gas near the bubble and far from the bubble will increase, diffusion will continue until the bubble has dissolved entirely.

In the following paragraphs the formation of bubbles will be discussed as well as two mechanisms which stabilise small bubbles against buoyancy and dissolution.

3.2.1 Cavitation

In a pure liquid with no contaminants the nucleation of a bubble can be described as the fracturing of the liquid. The tensile strength of the liquid must be overcome by the acoustic field to nucleate a bubble. This corresponds to homogeneous nucleation. When the tensile strength of a liquid is measured, the result is often far lower than values predicted by theory. This is because the liquid is weakened by contaminants and nucleation is heterogeneous. For the sonication of carbon nanotubes it is likely that the interface between the liquid and the nanotubes is a weak spot with a smaller cavitation thresholds. In conclusion, there exists a threshold pressure above which cavitation in the liquid starts. The value of this threshold depends on both the history of the liquid and the nature of the contaminants within the liquid. Thresholds as low as 1 bar for water are reported in literature, while for normal tap water a value of 9 bar is reported [18].

3.2.2 Variably Permeable Skin Model

The variable permeable skin model as proposed by Yount [19] assumes that a small bubble nucleus can be stabilised by organic, surface active impurities within the liquid. The skin is initially permeable and elastic and the bubble volume will change as a result of a varying applied external pressure. Only when the external pressure is increased sufficiently and the bubble has reached a minimum size, the skin of surface active contaminents becomes ”closed” and prevents a further decrease in bubble size.

Carbon nanotubes are strongly hydrophobic and suspensions of carbon nanotubes are often stabilised by adding surfactant to the suspension. There should be no shortage of surface active material in the suspension. The variable permeable skin model is a relevant mechanism for bubble stabilisation in the sonication experiment.

3.2.3 Crevices in Motes Model

Motes are micron sized particles suspended in the liquid and their movement is determined by Brownian motion. A bubble that would normally be removed from the system through its buoyancy, can be stabilised by attachment to such a mote. The average density of the mote and bubble combined is of the order where Brownian motion is dominant over gravitational effects. Again this mechanism depends on the presence of impurities within the liquid, if the liquid is filtered before sonication the number of motes should be low. Furthermore, this mechanism only explains the presence of pre-existing bubbles. It does not explain the formation of new bubble nuclei.

Crevices in a mote or in the surface of the sonication bath can cause the heterogeneous
nucleation of a bubble. The interface between the liquid and a bubble in a crevice can either be convex, flat or concave as shown in figure 6. Whether the surface is convex, flat or concave depends on the strength of the interactions between the liquid, the solid in which the crevice is situated and the gas phase of the liquid. If the mote is strongly hydrophobic the interface will be concave, the surface of the unfavourable solid-liquid interface is reduced. The concave interface between the liquid and bubble has a larger surface than a flat interface, the cost for reducing the area of the solid-liquid interface is an increase in the surface of the liquid-gas interface. The contact angle is that angle for which the total free energy of the liquid-solid, solid-gas and gas-liquid interface is at a minimum. The contact angle is determined by the type of liquid used and the material in which the crevice is situated.

![Diagram of bubble formation](image)

**Figure 6:** Four crevices in a mote. The first crevice is occupied by a bubble with a liquid-gas interface with positive radius of curvature. The bubble experiences a positive Laplace pressure, as a result gas will diffuse out of the bubble. In the second crevice the liquid-gas interface is flat. The Laplace pressure equals zero, there is no diffusion. The third crevice is occupied by a bubble with negative radius of curvature, the bubble experiences a negative Laplace pressure as a result gas will diffuse into the bubble. Above the last crevice a bubble has just split of, how a crevice can nucleate a bubble is discussed below.

When the gas-solid interface is least favourable a convex liquid-gas interface is obtained, the solid is hydrophilic if the liquid in which the mote is immersed is water. The convex interface has a positive radius of curvature as can be seen from the crevice on the left in figure 6. The Laplace pressure, as given by equation (4), has a positive value for the convex interface. Just as it does for a small bubble, the Laplace pressure results in the diffusion of gas out of the bubble contained in the crevice until it has dissolved. The second crevice in figure 6 shows a bubble with a flat liquid-gas interface. The radius of curvature approaches infinity and the Laplace pressure is zero, there is no diffusion. A concave liquid-gas interface will be obtained when the liquid-solid interface is least favourable. If the mote is immersed in water, the solid is hydrophobic. The liquid-gas interface has a negative radius of curvature as can be seen from the third crevice in figure 6. The Laplace pressure is negative and causes a diffusion of gas into the bubble. The bubble is stabilised against dissolution.

Consider a hydrophobic mote within a volume of water and let the mote contain numerous crevices. The interface between a bubble contained in a crevice and the water will have a negative radius of curvature as was explained above. If the local pressure within the liquid near the crevice is lowered by an acoustic field, the bubble will respond by changing its volume. As the local liquid pressure decreases, the interface will recede upwards until the top of the crevice is reached. If the local liquid pressure is decreased beyond this point, the
bubble is no longer contained by the crevice and the liquid-gas interface becomes convex. The Laplace pressure suddenly changes from a negative value to a positive value, there is no longer a quasistatic, mechanical, equilibrium between the bubble and the surrounding liquid. At this point it is more favourable to pinch of a bubble and let the remainder of the bubble regain the more favourable concave interface within the crevice.

The above is a simple, intuitive, argument which explains the nucleation of a bubble from a crevice. A more thorough discussion of the crevice model, in which a pressure threshold for bubble nucleation from a crevice is given, can be found in an article by Prosperetti [20]. The idea of a pressure threshold above which a bubble can be nucleated from a crevice is an interesting idea, it might help to explain the observed increase in the scission rate with increasing sonication power. A higher sonication power implies a higher pressure amplitude, which would in turn mean that a larger number of crevices can nucleate bubbles. This allows for an increase in the number of imploding bubbles per unit of time and as a result in an increase in the scission rate. Clearly this is just an intuitive argument, though a more detailed description would be interesting, it is beyond the scope of the present work.

The crevice model only works if there is a sufficient amount of gas dissolved in the liquid and if there is a sufficient amount of crevices available. As the sonication liquid is in contact with the air, a sufficient amount of gas should be dissolved in the water to allow for bubble nucleation from crevices. An interesting question in this regard is whether a carbon nanotube or a rope of nanotubes can contain a crevice from which bubbles can be nucleated or in which a bubble can be stabilised.

3.2.4 The bubble formation rate

Bubbles can be formed in crevices in motes or crevices in the walls of the sonication bath or at “weak spots” within the liquid. These weak spots are often formed by contaminants within the liquid. From the previous two paragraphs it is however not clear at what rate bubbles are nucleated by these mechanisms. It is very difficult to give such a number. The bubble formation rate will depend on the acoustic power and frequency, but also on the type of contaminants and crevices within the system. The latter depend strongly on the preparation of the sonication experiment. Once cavitation has started, the interaction of the acoustic field with the bubbles will strongly affect the acoustic field. This makes it even more difficult to derive a bubble formation rate. Instead of attempting to find an expression for it, we will just assume that the formation rate of bubbles, which can cause the scission of carbon nanotubes, is proportional to the acoustic power as is suggested by experiments [1].

3.3 Transient Cavitation

Both buoyancy and dissolution can be slow process compared to the process of transient cavitation. Once a bubble has formed it will have some time to interact with the imposed acoustic field before it dissolves or is removed from the liquid through buoyancy.

The dynamics of a bubble in an acoustic field can be approximated by the Rayleigh-Plesset equation. This equation is a non-linear equation of motion for the radius of the bubble, $R(t)$. The bubble is assumed to be surrounded by an incompressible, viscous liquid to which a time-varying acoustic field, $P(t)$, is applied for $t > 0$. Furthermore, the bubble is assumed
to be at rest and have a radius $R_0$ at $t \leq 0$. The Rayleigh-Plesset equation is:

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho} \left[ \left( p_0 + \frac{2\sigma}{R_0} - p_{v,b} \right) \left( \frac{R_0}{R} \right)^{3\kappa} + p_v - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} - p_0 - P(t) \right],$$  \hfill (6)

here $\rho$ is the mass density of the liquid, $\eta$ is the shear viscosity and $\kappa$ is the polytropic index. The polytropic index for a system is defined as $pV^\kappa = C$ with $C$ a constant. Essentially it is a measure of the degree to which the bubble behaves adiabatically, in which case $\kappa = \gamma$ and there is no heat flow into or out of the bubble, or isothermally in which case $\kappa = 1$ and there is an unhindered heat flow into and out of the bubble.

The numerical analyses of the Rayleigh-Plesset equation let to the discovery of two distinct types of response of a bubble to an acoustic field. Either the oscillations of a bubble in the acoustic field are stable, in which case it is considered as stable cavitation, or the oscillations are unstable and the bubble nucleus will experience explosive growth followed by a violent collapse. This is called transient cavitation. There exists both an upper and lower threshold bubble radius for transient cavitation. Only bubbles with a radius in between those thresholds can experience transient cavitation. Bubbles smaller than the lower threshold, the Blake threshold, will not experience explosive growth. Bubbles larger than the upper threshold, the Flynn dynamical radius cannot concentrate energy sufficiently to let the violent implosion occur. Both thresholds are discussed below.

Stable cavitation is not discussed in this report as it will not cause the scission of nanotubes. It is however important to realise that not all bubbles within a sonication bath will display violent, transient cavitation.

### 3.3.1 Explosive growth: Blake Threshold

The internal pressure of a bubble in equilibrium is the sum of the Laplace pressure and the liquid pressure just outside the bubble. If the liquid pressure is changed by the application of an acoustic field, the bubble will respond by changing its volume. The expansion of the bubble is however inhibited by surface tension, growth of the bubble is only possible when the acoustic pressure overcomes the surface tension. The pressure at which this happens is called the Blake Threshold, a derivation of the threshold can be found in appendix A. The Blake pressure, $p_B$, is a function of the initial bubble size, $R_0$:

$$\frac{p_B}{p_0} = 1 + \sqrt{\frac{4}{27} \left( \frac{p_0}{p_\xi} \right)^3 + \left( \frac{p_0}{p_\xi} \right)^2}, \quad \frac{2\sigma}{R_0} = \frac{2\sigma}{R_0 \sqrt{3 \left( 1 + \left( \frac{p_0 R_0}{2\sigma} \right) \right)}},$$  \hfill (7)

In appendix A, $p_B/p_0$ is plotted as a function of $p_0/p_\xi$ in figure 29. For a 10 W acoustic field the root mean square pressure amplitude is approximately 3.9 bar and the minimum bubble radius for explosive growth is approximately 0.2 µm. The Blake threshold is only valid when surface tension is dominant over viscous and inertial effects as neither of these effects are included in the calculation of the Blake threshold. This is the case when the bubble is smaller than the Minnaert resonance size. The acoustic field is then slow compared to the dynamics of the bubble, the bubble will have sufficient time to grow in a quasi static manner. For a bubble in water at 1 atmosphere the resonance radius, $R_r$, is given by:

$$R_r \nu = 3 \text{ ms}^{-1}.$$  \hfill (8)
Here $\nu$ is the frequency of the acoustic field. For a frequency of $\nu = 20$ kHz the resonance radius is then of the order of 0.15 mm. This is well above the radius of the bubble size at the Blake threshold, the obtained value of 0.2 $\mu$m can be used.

### 3.3.2 Flynn’s Dynamical Radius

There exists a critical ratio between the initial bubble size before explosive growth and the maximum bubble size obtained during explosive growth, if transient cavitation is to occur. The initial bubble size, before explosive growth, must at least be a factor 2.3 smaller. This maximum initial radius is known as Flynn’s dynamical radius. Only if the initial bubble is smaller, the collapse of the bubble will be dominated by inertial effects and the collapse will be a high-energy event, a more thorough discussion of this limit is beyond the scope of this report. To determine the maximum initial bubble radius for which transient collapse will still occur, we must determine the bubble radius which is obtained during explosive growth. Apfel [21] argued that the maximum radius, $R_{\text{max}}$, that a bubble will obtain during the explosive growth is approximately equal to:

$$R_{\text{max}} / R_\xi = \left(1 - \frac{p_0}{p_A}\right) \left(\frac{1}{3} + \frac{2}{3} \frac{p_A}{p_0}\right)^{1/3}, \quad R_\xi = \frac{4}{3\omega} \sqrt{\frac{2p_A}{\rho}}.$$  

(9)

Here $\omega$ is the frequency of the applied acoustic field. The derivation of this equation can be found in appendix B where a plot of this function is also shown. Using typical values for a sonication process, that is, a 10 W acoustic field with a frequency of $\nu = 20$ kHz and an amplitude of $p_A = 5.5 \cdot 10^5$ Pa, the maximum bubble size reached during the explosive growth is of the order of 0.5 mm. The initial radius of a bubble must at least be a factor 2.3 smaller than the maximum radius obtained during the explosive growth if transient cavitation is to occur. The maximum initial radius for transient cavitation is then of the order of 0.2 mm.

A closer look at those numbers suggests that the growth is explosive indeed. From the derivation of the maximum bubble radius we have an estimate of the average wall velocity during the explosive growth, $v = \sqrt{4(p_A - p_0) / (9\rho)}$. For a root-mean-square pressure of 4 bar, the average wall velocity is approximately 11 ms$^{-1}$. During the explosive growth the bubble expands from $2 \cdot 10^{-7}$ m to a radius of $5 \cdot 10^{-4}$ m, the radius increases by three orders of magnitude and the volume by $9^3$!

### 3.3.3 Bubble implosion

Lord Rayleigh first looked at the collapse of an empty spherical cavity within a fluid. He assumed that all the energy obtained from the expanding water volume is converted into kinetic energy of the water moving in to fill the cavity. The amount of work performed by the radially expanding volume of water is then given by:

$$p\Delta V = p_0 \cdot \frac{4}{3} \pi \left(R_{\text{max}}^3 - R^3\right).$$

(10)

If the effects of surface tension are neglected, $p_0$ is the constant liquid pressure just outside the bubble. The bubble radius as a function of time is given by $R$, the initial bubble radius is $R_{\text{max}}$. The energy generated by the expanding volume is converted into kinetic energy of the liquid moving in to fill the cavity. The kinetic energy of the liquid is given by:

$$E_{\text{kin}} = \frac{1}{2} \int R^2 dV.$$

(11)
Here, \( r \) is the radial distance from the centre of the bubble and \( \dot{r} \) the radial fluid velocity at a distance \( r \) from the middle of the bubble. By assuming incompressibility of the liquid, which implies \( R^2 \dot{R} = r^2 \dot{r} \), the total kinetic energy of the moving fluid can be determined. It is given by \( E_{\text{kin}} = 2\pi\rho R^3 \dot{R}^2 \).

By using the equality \( p\Delta V = E_{\text{kin}} \) a differential equation for the wall position is obtained:

\[
\dot{R} = v(R) = -\sqrt{\frac{2p}{3\rho} \left( \frac{R_{\text{max}}^3}{R^3} - 1 \right)}.
\]  

(12)

Note that the velocity of the bubble wall is zero for \( R = R_{\text{max}} \), this is in accordance with the starting condition. As the velocity of the bubble wall becomes negative for any reduction of the bubble radius below its initial maximum radius, any such reduction in the bubble radius will trigger the collapse of the bubble. This small initial decrease in bubble radius will occur instantly as the pressure outside the bubble is greater than the pressure in the bubble.

Finally, by again using the incompressibility of the liquid, the radial liquid velocity at a distance \( r \) from the middle of the bubble can be determined:

\[
v(r) = v = \frac{R^2 \dot{R}}{r^2} = -\frac{R^2}{r^2} \sqrt{\frac{2p}{3\rho} \left( \frac{R_{\text{max}}^3}{R^3} - 1 \right)}.
\]  

(13)

At some point during the implosion the receding bubble wall will reach the speed of sound, \( c \). The bubble radius at which this approximately happens is:

\[
R_c = R_{\text{max}} \left( \frac{2p}{3\rho c^2} \right)^{1/3}.
\]  

(14)

At this point the assumption that the fluid is incompressible becomes invalid and equations (6,12,13) are no longer valid as they were derived by assuming incompressibility. This is rather problematic as it is usually assumed that scission will occur during the final stages of collapse, during these stages the implosion will be supersonic.

Still, the equations can be used to estimate the strain rate just before the flow becomes supersonic. Rayleigh’s model for the collapse of an empty cavity gives a simple differential equation (12) for the bubble radius. A more advanced differential equation for the bubble radius is given by the Rayleigh-Plesset equation (6). Clearly, Rayleigh’s model neglects a fair number of influences on the behaviour of the bubble:

- The external pressure is assumed to be constant in time. In reality a harmonic acoustic field is applied;
- Surface tension is neglected, especially during the final stages of collapse the Laplace pressure should increase the speed of the implosion;
- Viscous effects are neglected;
- The internal bubble pressure is neglected;
- The system is assumed to be isothermal, this is not necessarily the case.
The differential equation for the bubble radius, equation (12) can be solved numerically. The used numerical method is discussed in appendix C. The differential equation was solved for a bubble with an initial radius of 0.5 mm and a pressure of 4.9 bar which corresponds to the sum of the root mean square pressure of a 10 W acoustic field plus the atmospheric pressure. In figure 7 the bubble radius and velocity of the bubble wall during collapse are plotted.

### Figure 7: The left graph shows the bubble radius as a function of time during collapse, the right graph shows the velocity of the bubble wall. The bubble considered has an initial radius of 0.5 mm and the liquid pressure is 4.9 bar.

In the final stages of the collapse, the velocity of the bubble wall approaches infinity. This is not surprising as the differential equation shows that \( \dot{R} \propto R^{-3/2} \) for \( R << R_{\text{max}} \). In reality, the velocity cannot increase towards infinity and any gas within the bubble will cushion the collapse in the final stages, reducing the velocity of the bubble wall. Though the velocity should increase strongly in the final stages of collapse, it is unclear how much of the increase in velocity for \( t > 21 \mu s \) is the result of the approximations made in Rayleigh’s model and how much can be attributed to the actual physics involved. The bubble radius and implosion velocity as shown in figure 7 will be used throughout chapter 4, clearly the results for \( t > 21 \mu s \) should be regarded with some care.

The speed of sound in water under ambient conditions is approximately 1500 ms\(^{-1}\). This speed is only reached in the final stage of collapse as the velocity approaches infinity. For the situation considered in figure 7, the bubble radius at which the implosion becomes supersonic, as given by equation (14) is 28 \( \mu \)m, this radius is obtained at \( t = 22.4 \mu s \) after the start of the collapse. We will however use \( t = 21 \mu s \) as an approximation for the time up to which we consider Rayleigh’s model to be applicable to the transient collapse of a bubble.

As a final note, it is possible to obtain an analytical approximation for the bubble radius as a function of time, based on the differential equation as given by equation (12). The interaction between a nanotube and bubble as presented in the next chapter can then be analysed analytically. This analytic analysis will be part of future work.

### 3.3.4 Final stages of collapse

During the final stages of collapse the velocity of the bubble wall becomes supersonic. The theory as discussed in the previous paragraphs is no longer valid. These final stages of collapse are very violent, temperatures of the order of 5000 K are reached and light is produced [4]. The latter process, sonoluminescence is still poorly understood.
In paragraph 4.2 it is discussed how the thermal effects that occur during these final stages of collapse will affect a carbon nanotube. Fortunately it will turn out that the thermal effects do not affect the nanotubes as a nanotube cannot get sufficiently close to these effects to be affected.
4 Scission mechanics

In this chapter a simple model for the scission of carbon nanotubes due to the transient collapse of a bubble in an acoustic field is discussed. In chapter 3 the transient collapse of a bubble was discussed while in chapter 2 the mechanical properties of carbon nanotubes were discussed, the results from these chapters will be used in constructing the mechanical model for the scission of the nanotubes. In this model, the carbon nanotubes will be considered as a rigid rod-like particle, so they cannot bend. This is a reasonable assumption as long as the nanotubes considered have a length shorter than the persistence length of a nanotube. A persistence length of 32 $\mu$m up to 174 $\mu$m is reported for single-wall nanotubes [9]. The persistence length of a defect-free, multi-wall nanotube should be even higher.

The nanotube will attain a radial alignment in a radial inward flow following the collapse of a bubble. This is easily seen from picture 8. The carbon nanotube will be dragged along at a radial velocity $v_{\text{cnt}}$ by the fluid. This results in a relative fluid velocity, $v_{\text{rel}}$, along the nanotube. This velocity will be radial inward at the part closest to the bubble (part 1) and outward on the part furthest away from the bubble (part 2). The viscous drag forces on the nanotube, $F_1, F_2$, will then apply a torque on the nanotube if it is not radially aligned. The direction and magnitude of these forces is derived in the next paragraph. The torque resulting from these forces will enforce a radial alignment of the nanotube.

![Figure 8: A schematic representation of a carbon nanotube moving radially inward at a velocity of $v_{\text{cnt}}$. The nanotube on the left is not aligned radially. The relative fluid velocity results in viscous drag forces along the nanotube with magnitude, $F_1, F_2$. These forces apply a torque on the nanotube which tend to align it radially. The nanotube on the right is radially aligned. The picture is explained in more detail in paragraph 4.1.](image)

4.1 Fluid friction on a carbon nanotube

The friction between a section of a radially aligned carbon nanotube and the radial flow following the implosion of a bubble is proportional to the product of the relative fluid velocity, $v_{\text{rel}}(r)$, and the viscosity of the fluid, $\eta$. Remarkably, the dependence on the diameter of the nanotube is negligible, the dependence is only logarithmic. Following Hennrich et al.
and neglecting the logarithmic correction for nanotube diameter, the radial component of the viscous drag forces per unit length are approximately equal to:

\[ f_{\text{vis}}(r) = 2\pi \eta v_{\text{rel}}(r). \]  

(15)

The radial flow, \( v(r) \), will accelerate the nanotube and drag it along at a speed \( v_{\text{cnt}} \). The velocity of the carbon nanotube can be derived by assuming mechanical equilibrium, the total force the fluid exerts on the carbon nanotube is zero. The force per unit length exerted on the carbon nanotube is given by equation (15), where \( v_{\text{rel}}(r) = v(r) - v_{\text{cnt}} \) is a radial velocity.

Figure 9: A radially aligned carbon nanotube with its leading edge at a distance \( r_c \) from the middle of the imploding bubble. The imploding bubble has a radius \( R \).

In figure 8 and 9 the situation is sketched. Shown in these pictures is a radially aligned carbon nanotube of length \( L \) at a distance \( r_c \) from the centre of the bubble. Along the carbon nanotube there is a point \( r^* \) where the relative fluid velocity is zero, here the radial velocity of the carbon nanotube is equal to the velocity of the fluid flow, \( v(r^*) = v_{\text{cnt}} \). Define the section of the carbon nanotube with \( r < r^* \) as part one, the relative fluid velocity is inward. The total radial force exerted by the fluid on this section is \( F_1 \). Part two of the nanotube is then the part with \( r > r^* \), the relative fluid velocity is outward. The total radial force exerted by the fluid on it is \( F_2 \). In mechanical equilibrium the total force on a nanotube is zero, so \( F_1 + F_2 = 0 \), the radial forces \( F_1 \) and \( F_2 \) are given by:

\[ F_1 = \int_{r_c}^{r^*} f_{\text{vis}}(r) \, dr, \quad F_2 = \int_{r^*}^{r_c+L} f_{\text{vis}}(r) \, dr. \]  

(16)

From the criterium for mechanical equilibrium the radial velocity of a carbon nanotube at a distance \( r_c \) from the centre of the bubble can now be derived:

\[ v_{\text{cnt}} = \frac{1}{L} \int_{r_c}^{r_c+L} v(r) \, dr. \]  

(17)
The radial velocity of the carbon nanotube is equal to the average radial fluid velocity, \( v(r) \), along the carbon nanotube.

Knowing the velocity of the carbon nanotube, the normal stress on a segment of the carbon nanotube at position \( r \) can be determined. Again the nanotube can be divided into two sections, the first from \( r_c \) up to \( r \) and the second from \( r \) up to \( r_c + L \). The normal stress on this segment is the total force on the first section, minus the total force acting on the second section divided by the surface of the cross section of the nanotube. The force on the first section, minus the force on the second section is given by:

\[
F(r) = \int_{r_c}^{r} f_{vis}(r') \, dr' - \int_{r}^{r_c+L} f_{vis}(r') \, dr' = 4\pi \eta \int_{r_c}^{r} v_{rel}(r') \, dr'.
\]  

(18)

The total force is twice the force on the first section. This is not surprising, mechanical equilibrium requires that the total force on the carbon nanotube equals zero. So, independent of the value of \( r \), the force on the first section plus the force on the second section must equal zero: \( F_1 = -F_2 \) so \( F_1 - F_2 = 2 \cdot F_1 \). This is true, regardless of the actual radial flow profile. The surface of the cross section of the carbon nanotube, \( \pi d^2/4 \), is constant, so the position \( r^* \) where the normal stress reaches a maximum is given by the position where \( F(r) \) reaches its maximum value:

\[
\frac{\partial F(r)}{\partial r} = 0 \quad \rightarrow \quad v(r) = v_{cnt} \quad \rightarrow \quad r = r^*.
\]  

(19)

The normal stress reaches a maximum value at \( r = r^* \), where the relative fluid velocity is zero. The maximum stress at this position is given by:

\[
\sigma_{max} = \frac{8\eta}{d^2} \int_{r_c}^{r^*} v_{rel}(r) \, dr.
\]  

(20)

The carbon nanotube will break if \( \sigma_{max} > \sigma_b \). The tensile strength, \( \sigma_b \), of a carbon nanotube was discussed in paragraph 2.2 and is of the order of \( 10^{10} \) Pa.

### 4.2 Interaction between a nanotube and an imploding bubble

In the previous paragraph, the interaction between a carbon nanotube and a radial inward flow was discussed. Equations for the carbon nanotube velocity, equation (17), and the maximum stress experienced by the nanotube, equation (20), were derived. In this paragraph these equations will be applied to the flow following the collapse of an empty bubble in an incompressible liquid as derived by Rayleigh and discussed in paragraph 3.3.3. Remember that for the final stages of collapse the velocity of the implosion will approach infinity, clearly this cannot be correct. Any result shown for \( t > 21 \) \( \mu \)s should be considered with some care as it is not clear whether it should be attributed to the mathematical details of the model or to the actual physics involved in transient cavitation.

#### 4.2.1 Nanotube velocity

In Raleighs model the radial liquid velocity at a distance \( r \) from the centre of a bubble is determined by equations (12, 13). The position of the bubble wall was determined as a
function of time by solving the differential equation as given by equation (12). A solution was obtained in paragraph 3.3.3 for a bubble with an initial bubble radius of 0.5 mm and an external liquid pressure of 4.9 bar, it is shown in figure 7. With the bubble radius $R$ known as a function of time, the full liquid flow is known if the liquid is assumed to be incompressible. The radial liquid velocity is given by:

$$v(r) = -\frac{R^2}{r^2} \sqrt{\frac{2p}{3\rho} \left( \frac{R_{\text{max}}^3}{R^3} - 1 \right)}.$$  \hfill (21)

From equation (17) the speed at which a carbon nanotube is dragged along by the fluid can now be determined. The velocity of the carbon nanotube depends on its length, $L$, and the distance between the bubble and the nanotube just before the start of the implosion.

What is clear, is that the velocity of the nanotube must always be lower than the velocity of the bubble wall. Remember the velocity of the carbon nanotube is equal to the average fluid velocity along the nanotube, the latter decreases as $r^{-2}$. The distance between the bubble wall and nanotube should then increase as the collapse progresses. In the right graph in figure 10 the distance between the bubble wall and carbon nanotubes of various lengths (10, 50, 100, 500 and 1000 nm) is plotted as a function of time. In making these plots it was assumed that the carbon nanotube starts out radially aligned and with its leading edge right at the bubble wall, $r_c(t=0) = R_{\text{max}}$, the numerical method used to obtain this plot is briefly discussed in appendix D.

![Graphs](image)

Figure 10: The left graph shows the bubble radius as a function of time during the collapse. The right graph shows the distance between the bubble wall and a carbon nanotube of 10, 50, 100, 500 and 1000nm. Both plots are based on results from Rayleigh’s model for the collapse of an empty cavity as is formed in a typical sonication experiment, that is, a 10 W, 20 kHz acoustic field applied to a volume of water.

The plot shows that at the end of the collapse a nanotube of 10 nm or longer is at a distance of the order of 50 µm from the centre of the bubble. Furthermore the graph shows that the distance between the bubble wall and a nanotube will increase faster for longer nanotubes. Perhaps the most important conclusion from the graph is that nanotubes will be too far from the bubble centre to be affected by the strong thermal effects which occur during the final stages of collapse. Temperatures of the order of the melting temperature of graphene (almost 5000 K) are reached in the region up to 200 nm from the bubble centre [23]. This could lead to the melting of carbon nanotubes if the nanotube were to be sufficiently close to the centre of the implosion. From figure 10 it is clear that the nanotubes are at a distance of 50 µm
from these effects and are as a result not affected.

Especially in the final stages of collapse, \( t > 21 \mu s \), the velocity of the nanotube becomes much smaller than the velocity of the bubble wall and the distance between the bubble wall and nanotube increases strongly. Though the implosion is poorly modeled by Rayleighs model during the final stages of collapse, the result seems credible. The velocity of the nanotube is equal to the average fluid velocity along its length, so the higher the shear rate of the flow the greater the difference between the velocity of the nanotube and the bubble wall. Equation (32) shows that the shear rate is proportional to \( 1/r \) for an incompressible fluid, so indeed the closer the nanotube gets to the centre of the implosion, the slower it will be compared to the bubble wall and the faster the distance between the bubble wall and nanotube will increase. This explains the strong increase in distance between the nanotube and bubble wall for \( t > 21 \mu s \).

4.2.2 Maximum stress

The radial fluid flow is given by equation (21), this equation is of the form:

\[
v(r, t) = A(t) r^{-2}, \quad A(t) = -R(t)^2 \sqrt{\frac{2p}{3\rho}} \left( \frac{R_{\text{max}}^3}{R(t)^3} - 1 \right). \tag{22}
\]

From equations (17, 19), the position where the stress on the nanotube reaches a maximum can be determined. It is easily shown that this position is given by:

\[
r^* = \sqrt{r_c (r_c + L)}. \tag{23}
\]

The relative breaking position is then given by: \((r^* - r_c)/L\), here a value of 0.5 corresponds to scission right at the middle of the nanotube. Whether the nanotube will break is determined by the maximum stress (equation (20)). For the inward flow as given by equation (22) the maximum stress reached at \( r = r^* \) is:

\[
\sigma_{\text{max}} = \frac{8\eta R^2 \dot{R}}{d^2} \left[ \frac{1}{\sqrt{r_c}} - \frac{1}{\sqrt{r_c + L}} \right]^2. \tag{24}
\]

Note that \( r_c \) is a function of time, \( r_c = r_c(t) \). Equations (23, 24) are in agreement with what was derived by Terentjev et al. [23].

The maximum tensile stress and the position where it is reached can now be determined for nanotubes of various length as a function of time, the maximum stress and relative breaking position are shown in figure 11. The bubble radius and position of the nanotube as shown in figure 10 were used, this plot was obtained by considering the collapse of a bubble in water to which a 10 W and 20 kHz acoustic field is applied. The relative breaking position and maximum tensile stress are plotted as a function of time in figure 11, the colours in each of the plots correspond to a nanotube of the same length.

A nanotube diameter of 10 nm and a viscosity of \( \eta = 10^{-3} \) Pa/s are used to determine the maximum value of the stress in figure 11. The maximum stress exerted on a nanotube is of the order of \( 10^8 \) Pa for a nanotube of 1 \( \mu \)m, a value two orders below the tensile strength of a carbon nanotube. The model does not explain the scission of a carbon nanotube.
The bubble dynamics were however poorly modeled by Rayleigh’s model for the collapse of an empty cavity. The acoustic field was approximated by the root mean square pressure of the acoustic field, in reality higher pressures are reached during the collapse. Furthermore, the effects of surface tension were not included. Both factors should increase the speed of collapse during the final stages.

![Graphs showing relative breaking position and maximum stress over time.](image)

Figure 11: *The left graph shows the relative breaking position as a function of time during the collapse. The right graph shows the maximum stress as a function of time. The quantities are again plotted for carbon nanotube of 10, 50, 100, 500 and 1000 nm, each colour represents the same nanotube length as in the left graph. These graphs were obtained by considering the collapse of an empty cavity in a typical sonication experiment (water, 10 W acoustic field with a frequency of 20 kHz).*

Finally, the highest levels of stress are reached during the final stages of collapse. From figure 7 it is clear that the flow becomes supersonic during these stages. The flow is however modeled by subsonic physics, which is obviously not correct. Perhaps the inclusion of supersonic physics, a time-dependent acoustic field and the effects of surface tension in our model will increase the stress experienced by nanotubes to a value above the tensile strength of the nanotube.

The left plot shows that the maximum stress is reached almost exactly at the middle of the nanotube. The two segments in which the nanotube breaks can be considered to be of equal length. That scission occurs right at the middle is very useful in describing the scission process as a consecutive process, the mathematics of such a process is discussed in chapter 5. In paragraph 4.3 it will be shown that the relative fluid velocity along a nanotube is approximately linear, for a linear flow, scission will always occur at the middle.

### 4.2.3 The scission rate as a function of nanotube length

In the previous paragraph transient cavitation was modeled by Rayleigh’s model for the collapse of an empty cavity. In paragraph 3.3.3 the shortcomings of this model were discussed and from the previous paragraph it is clear that the model does not result in a sufficiently high stress on the nanotube to cause the scission of it. In this paragraph we will consider a fictitious nanotube with a diameter of 10 nm and a tensile strength of just $5 \cdot 10^6$ Pa, a value four orders of magnitude below the actual tensile strength of a nanotube.

The scission rate is a measure of the probability that a nanotube will break within an in-
terval of a unit time. The nanotube will break if the stress exerted on the nanotube during the collapse of the bubble is larger than its tensile strength. The stress at (approximately) the middle of the nanotube is given by equation (24). Here $R, \dot{R}$ and $r_c$ are all functions of time, $r_c$ is also a function of the nanotube length, $L$, and its position before the start of the collapse, $r_c(0)$. The further the nanotube is initially removed from the centre of the bubble the smaller the stress it will experience during the collapse of the bubble. That this is indeed the case can be seen from figure 12 where the stress at the middle of the nanotube at $t = 21\mu s$ is shown as a function of nanotube length and its initial distance from the bubble.

There exists a maximum initial distance from the centre of the bubble for which the maximum stress exerted on the nanotube is equal to its tensile strength. If the nanotube is at a greater distance from the bubble at the start of the transient collapse of the bubble it will not break. This maximum distance, $r_{c,\text{max}}(L)$, depends on the nanotube length. In the left graph in figure 12 the stress on a nanotube of length 1000, 900, 800, ..., 100 nm at $t = 21\mu s$ during the transient collapse of a bubble in a 20 kHz and 10 W acoustic field is shown as a function of its initial distance from the centre of the bubble, $r_c(0)$.

![Figure 12: The left graph shows the stress on a nanotube of length 1000, 900, 800, ..., 100 nm at $t = 21\mu s$ as a function of its initial distance from the bubble centre. The top purple curve corresponds to the 1000 nm nanotube while the bottom blue curve corresponds to a 100 nm nanotube. The black line at a stress of $5 \cdot 10^6$ Pa corresponds to the tensile strength. The right graph shows the maximum initial distance, $r_{c,\text{max}}$ as a function of nanotube length](image)

The initial position is expressed in units of the bubble radius just before collapse, the bubble radius is then $R_{\text{max}} = 0.5$ mm. The stress on the nanotube with a length of 100 nm never exceeds the (fictitious) tensile strength of $5 \cdot 10^6$ Pa, not even if it starts right at the bubble wall. It cannot be broken during sonication. For the longer nanotubes the stress will exceed the tensile strength if the nanotube starts sufficiently close to the bubble. The maximum initial distance from the bubble centre for which scission will occur, $r_{c,\text{max}}(L)$, can be determined from this graph, per nanotube length it is equal to the $x$ value where the corresponding curve crosses the line $y = 5 \cdot 10^6$. The right graph in figure 12 shows this maximum initial distance as a function of nanotube length. The maximum initial distance appears to increase linear with nanotube length, a linear “fit” is shown in the right graph it is given by:

$$r_{c,\text{max}}(L) = R_{\text{max}} \left( 0.77 + 10^6 \cdot L \right).$$

(25)

The shortest nanotube which will be broken by sonication is given by $r_{c,\text{max}}(L) = R_{\text{max}}$, the minimum length for scission to occur is then 230 nm.
If we assume that a bubble grows from a small initial size to its maximum size, \( R_{\text{max}} = 0.5 \) mm just before the start of the collapse. Then any nanotube of length \( L \) that is located within a radial distance between the initial bubble radius and the maximum initial distance from the centre of the bubble, \( r_{c,\text{max}} (L) \), at the moment the explosive growth of the bubble starts will break. The initial size of a bubble before explosive growth varies between 0.2 \( \mu \)m (Blake threshold, see paragraph 3.3.1) and 2.3 mm (Flynn’s dynamical radius, see paragraph 3.3.2). If the initial radius of the bubble before explosive growth is of the order of the Blake radius, the initial volume of the bubble is negligible compared to its volume after explosive growth. Then per bubble that will display transient collapse there is a volume \( V(L) \) around the centre of the bubble for which any nanotube of length \( L \) in it will break:

\[
V(L) = \frac{4}{3} \pi (r_{c,\text{max}} (L))^3. \tag{26}
\]

As discussed in chapter 3, experiments suggest that the number of transient bubbles is proportional to the acoustic power supplied to the system [1]:

\[
N_B \propto P_{\text{ac}}. \tag{27}
\]

Here \( N_B \) is the number of bubbles that will display transient collapse per unit volume per unit time. For a nanotube of length \( L \) a fraction of \( N_B \cdot V(L) \) of each unit volume corresponds to the region in which any nanotube of that length will break within a unit of time.

Let \( x(L) \) be the concentration of nanotubes of length \( L \), then per unit volume and time a total of \( N_B \cdot V(L) \cdot x(L) \) nanotubes of length \( L \) will break. This number should be equal to the product of the scission rate, \( k(L) \), and the nanotube concentration. The scission rate is then:

\[
k(L) = k \cdot P_{\text{ac}} \cdot \frac{4}{3} \pi R_{\text{max}}^3 \cdot (0.77 + 10^6 \cdot L)^3, \quad L > 230 \cdot 10^{-9} \text{m}. \tag{28}
\]

Here \( k \) is an unknown constant of proportionality between the number of transient bubbles and the acoustic power (equation (27)). Finally, there will be a nanotube length for which the volume \( V(L) \) around one bubble will start to overlap with the same volume around a neighbouring bubble. At this point the volume fraction for which scission will occur no longer increases. The scission rate will no longer increase and remain constant. The nanotube length at which this will happen depends on the concentration of transient bubbles, \( N_B \), and is as a result unknown.

In figure 13 the scission rate is shown in a log-log plot as a function of nanotube length. The red dot corresponds to the minimum length of 230 nm for which scission will occur, note that this minimum length depends, among others, on the applied acoustic field, the tensile strength of a nanotube and the diameter of a nanotube. The point where the scission rate levels off to a constant value was chosen arbitrarily.

For nanotube lengths of 1 \( \mu \)m or more the scission rate increases with \( L^3 \). This dependence on length can be used as a crude approximation of the scission rate for all lengths above the minimum length for scission. The power-law approximation for the scission rate is:

\[
k(L) = k'L^3. \tag{29}
\]

Here \( k' \) is a constant of proportionality which is different in value from the one used in equation (28), its value depends on the frequency and power of the applied acoustic field. Note
that for smaller lengths the scission rate increases less strongly with increasing length than the power-law approximation suggests. Our model indicates that the maximum value of the exponent in the power-law approximation is 3 while smaller values should be used for shorter nanotubes.

![Figure 13: A double logarithmic plot of the scission rate as a function of nanotube length. The red dot shows the minimum nanotube length for scission to occur. For large nanotube length the scission rate becomes constant, the point at which this happens was chosen arbitrarily.](image)

This result is in contradiction with the results obtained by Poluin et al. [1] who find a value of 5 for the exponent. Hennrich et al. [22] find an exponent of 2, though smaller than 3, it is not in disagreement with our model.

Two important remarks must be made at this point, first the scission rate was derived for a fictitious nanotube with a tensile strength four orders smaller than that of a real nanotube. This was nessecary as Rayleighs model for the collapse of an empty cavity is too simple to explain the scission of a real nanotube. Second, the stress was determined at $t = 21 \mu s$ which is an arbitrary moment, the maximum stress is reached at a later moment, but it is doubtful whether Rayleighs model is still valid at this moment.

In conclusion, a more advanced model for the collapse of a bubble should be used to derive the scission rate for actual nanotubes in the same manner as was done in this paragraph.

4.3 Linear flow

In literature, the fluid flow following the collapse of a bubble is often approximated by a single strain rate [1], [22], the flow around the nanotube is assumed to be approximately linear. If this is indeed the case, a first order Taylor expansion of equation (22) should be a good approximation of the flow around the nanotube. A second order expansion around $r = r'$ is given by:

$$v(r) \approx v(r') \left[ 1 - \frac{2(r - r')}{r'} + \frac{3(r - r')^2}{r'^2} \right] + O \left( (r - r')^3 \right).$$

(30)

Let $r'$ be the distance from the centre of the bubble to the middle of the nanotube, figure 10 suggests that this distance is of the order of 10 $\mu m$ or more. A typical value for $(r - r')$ is of the order of half the nanotube length, say about 100 nm. The first order term in the
Taylor expansion is then two orders of magnitude smaller than the zeroth order term, while the second order term is already four orders smaller than the zeroth order term and can be neglected. The first order Taylor expansion around $r = r'$ is given by:

$$v(r) \approx v(r') \left[ 3 - \frac{2r}{r'} \right]. \quad (31)$$

The shear rate of the fluid flow around the nanotube is then given by:

$$\dot{\varepsilon} = 2v(r') / r'. \quad (32)$$

Theoretical predictions for the shear rate around an imploding bubble are as high as $1 \cdot 10^9$ s$^{-1}$. Experiments suggest an even higher value of $6 \cdot 10^9$ s$^{-1}$ up to $10^{10}$ s$^{-1}$ [1]. From figure 11 we know that the nanotubes do not get closer than approximately $50 \mu m$ from the centre of the implosion. Using this as a value for $r'$ in equation (32) suggests that the fluid velocity must be equal to $1.5 \cdot 10^5$ ms$^{-1}$ to obtain a shear rate of $6 \cdot 10^9$ s$^{-1}$. It is very unlikely that such a velocity is reached during the implosion, it corresponds to a Mach number of 100! Note that closer to the bubble wall a higher shear rate is reached, using a value of $r' = 10^{-6}$ m, a fluid velocity of $3000$ ms$^{-1}$ ‘just’ twice the speed of sound is required to obtain a shear rate of $6 \cdot 10^9$ s$^{-1}$. The problem is that our calculations indicate that the nanotube does not get this close to the centre of the bubble. At this moment it is unclear whether the modeling of the implosion by the full Rayleigh-Plesset equation or a supersonic treatment of the implosion will result in a sufficiently high shear rate to cause scission of a nanotube.

In figure 14 the shear rate at the bubble wall is shown as a function of time, during the final stages of collapse values of the order of $10^9$ are reached. This is a value of the same order of magnitude as is commonly reported in literature. However, the modeling of the implosion is poor in these stages of collapse.

![Figure 14: The strain rate at the bubble wall, $2v(R)/R$, is shown as a function of time.](image)

If the fluid flow along the nanotube is approximated by the first order Taylor expansion, equation 31, then the velocity of the nanotube (equation (17)), the position where the maximum stress is reached (equation (19)) and the magnitude of the stress (equation (20)) can be determined. The velocity of a nanotube in a linear flow is again equal to the average velocity along the nanotube, see equation (17). The nanotube velocity is then:

$$v_{cnt} = v \left( r_c + L/2 \right). \quad (33)$$
The relative fluid velocity is \( v(r) - v_{\text{cnt}} \). It is then easily shown that the maximum stress is reached exactly at the middle of the nanotube (equation (19)), the maximum stress reached at this point is (equation (20)):

\[
\sigma_{\text{max}} = \frac{2\eta \dot{\varepsilon} L^2}{d^2}.
\]  

(34)

The minimum length at which scission will still occur is then given by:

\[
L_{\text{min}} = \sqrt{\frac{d^2 \sigma_b}{2\eta \dot{\varepsilon}}}. 
\]  

(35)

For a nanotube with a 10 nm diameter and a tensile strength of \( \sigma_b = 10^{10} \) Pa and a shear rate of \( \dot{\varepsilon} = 10^{10} \) s\(^{-1}\) the minimum length at which scission will still occur is 220 nm. The shortest nanotube segments produced by sonication with a 10 W, 20 kHz acoustic field, in water is then 110 nm. This terminal length is in agreement with values reported in literature [1],[22], this is not surprising as the terminal length in these publications was determined with the same equation (35).

### 4.4 Defects & Scission dynamics

In paragraph 2.3 the different types of defects in a nanotube were discussed shortly. It was assumed that defects will locally lower the tensile strength of a nanotube. If the defect is not located at the middle of the nanotube and if it locally lowers the tensile strength sufficiently, the nanotube will break at the position of this defect instead of the middle. The stress on the defect will equal the locally reduced tensile strength before the stress at the middle of the nanotube reaches the tensile strength of a defect free nanotube. The degree by which the tensile strength must be reduced by the defect, if scission is to occur at the defect location, will depend on the position of the defect on the nanotube. For increasing distance from the middle of the nanotube the defect will have to locally decrease the tensile strength more and more.

If there are multiple defects on a single nanotube, scission at the defect closest to the middle of the nanotube will be favoured as the stress experienced by a nanotube segment will increase as the segments is located closer to the middle. This is easily seen from equation (36), using the linear approximation introduced in the previous paragraph, the stress experienced at a position \( x = (r - r_c)/L \) on a nanotube is given by:

\[
\sigma (x) = \frac{8\eta \dot{\varepsilon} L^2}{d^2} \left[ x - x^2 \right].
\]  

(36)

Assume a homogeneous distribution of defects over the nanotube, a typical number of defects on a nanotube per unit length and a typical decrease in tensile strength as a result of the defect. Based on these assumptions it should be possible, though most likely not easy, to derive an average break position of the nanotube. This position will not be at the middle of the nanotube. Scission at a defect will result in a short and a long segment, the average length of these two segments is still half that of the nanotube that breaks.

This non midtube scission will slow down the scission process if the scission rate is assumed to be a power-law function of nanotube length.

\[
k(L) = k L^\alpha.
\]  

(37)
Let the position where the nanotube breaks be given by \( x_B = (r_B - r_c)/L \), a value of \( x_B = 0.5 \) corresponds to the middle of the nanotube. The scission will result in a segment with length \( x_B L \) and a segment with length \( (1 - x_B) L \), the scission rate for each of these segments respectively is:

\[
k_1 = k (x_B L)^\alpha, \quad k_2 = k ((1 - x_B) L)^\alpha.
\]  
(38)

The typical time after which segment one will break is \( k_1^{-1} \), for segment two this typical time is \( k_2^{-1} \). The average time after which one of these segments will have broken is then \( (k_1^{-1} + k_2^{-1}) / 2 \). The average scission rate for these two segments, \( \bar{k} \), is given by:

\[
\frac{1}{\bar{k}} = \frac{1}{2} \left( \frac{1}{k_1} + \frac{1}{k_2} \right).
\]  
(39)

If the scission rate has a power-law dependence on nanotube length, the average scission rate of the two segments obtained by non midtube scission will be given by:

\[
\bar{k} = 2kL^{\alpha} \frac{x_B^\alpha (1 - x_B)^\alpha}{x_B^\alpha + (1 - x_B)^\alpha}.
\]  
(40)

In figure 15 the average scission rate is shown as a function of \( x_B \) for \( \alpha = 3 \), the value which was derived in paragraph 4.2.3.

![Figure 15: The average scission rate (equation (40)) as a function of the position \( x_B \) where the nanotube will break.](image)

The scission rate is given in units of the scission rate for midtube scission. The scission rate has a maximum at \( x_B = 0.5 \) which corresponds to scission at the middle of the nanotube. The average scission rate of the two segments of a broken nanotube decreases as the scission position moves away from the middle. The smaller the scission rate, the slower the scission process. In other words, the presence of defects can cause non-midtube scission which in turn will slow down the scission process.

The role of defects might help to explain the variety of exponents found in literature (as discussed in paragraph 4.2.3), the slowing down of the scission process due to defects should be stronger for nanotubes with more and greater defects.
5 Mathematics of a series of consecutive first-order reactions

In the introduction it was explained how the scission of nanotubes during sonication is a consecutive process. A single, long nanotube can break into two pieces and each of these pieces can break again and so on; it is a consecutive process. In paragraph 4.2.2 and 4.3 it was shown that a nanotube will generally break into two equal pieces, each half the length of the initial nanotube. This scission process can be represented by the following 'chemical' equation, \( A \rightarrow 2B \). Here, \( A \) represents the initial nanotube and \( B \) represents a nanotube with half the length of nanotube \( A \). If the nanotube represented by \( B \) is sufficiently long it can break again. This consecutive process of breaking stops when the nanotubes reach a minimum length, this length was derived in paragraph 4.3.

What follows is a mathematical treatment of a series of consecutive first-order reactions. The distribution of ‘particles’ over the consecutive states will be represented by a probability distribution, the mean value and standard deviation of the distribution will be derived. In the introduction it was mentioned that experimental results suggest that the distribution should display dynamical scale invariance, in paragraphs 5.4 and 5.5 the possibility of dynamical scale invariance in the distribution will be investigated. Where possible, results will be coupled to the topic of this report, the scission of carbon nanotubes under sonication. The results obtained in this chapter will be applied to the scission of carbon nanotubes in chapter 6. When important results from this chapter are used in chapter 6, a reference to the corresponding paragraph or equation in this chapter will be made. If not interested in the mathematics discussed in this chapter, the reader can skip this chapter altogether.

A first-order reaction is a reaction where only a single reactant (\( A \)) is required for the reaction while the reaction can have multiple products. However, we will only consider reactions with a single product (\( B \)), a single reactant particle can however produce multiple, \( m \), identical product particles. Such a reaction is represented by the following chemical equation:

\[
A \rightarrow mB. \tag{41}
\]

In the series of consecutive reactions the product of the first reaction is the reactant for the second reaction in the series and so on. If the first reactant is written as \( C_1 \) and the first product, which is the reactant of the second reaction, is written as \( C_2 \) and so on. Then a series of \( n \) consecutive first-order reactions can be expressed by the following chemical equation:

\[
C_1 \xrightarrow{k_1} m \cdot C_2 \xrightarrow{k_2} m^2 \cdot C_3 \xrightarrow{k_3} \ldots \xrightarrow{k_{n-1}} m^{n-1} \cdot C_n \xrightarrow{k_n} m^n C_{n+1}. \tag{42}
\]

Here \( k_i \) is the reaction rate of the \( i^{th} \) reaction. For the consecutive scission of nanotubes \( C_i \) would correspond to a nanotube with a length of \( L \cdot 2^{1-i} \) where \( L \) is the length of the nanotube represented by \( C_1 \) and \( k_i \) corresponds to the scission rate of the nanotube represented by \( C_i \). In paragraph 4.2.3 a length-dependent scission rate was derived for the scission of nanotubes under sonication.

If the time dependent concentration of \( C_i \) is written as \( x_i(t) \), then \( x_i(t) \) has to be a solution of the following set of differential equations:

\[
\begin{align*}
\dot{x}_1 &= -k_1 x_1, \\
\dot{x}_i &= m k_{i-1} x_{i-1} - k_i x_i, \quad 1 < i \leq n, \\
\dot{x}_{n+1} &= m k_n x_n.
\end{align*}
\tag{43}
\]
Here \( \dot{x} = dx/dt \). This set of linear differential equations has an exact solution which was first obtained for \( m = 1 \) by Sheppard in 1962. We retrieved the solution from an article published by R.C. Bailey in 1974 [24] and adapted the solution to accommodate for cases where \( m \neq 1 \).

If the starting conditions are given by \( \{ x_1(0), x_2(0), ..., x_{n+1}(0) \} \) and if each of the reaction rates \( k_i \) is assumed to be independent of the concentration of any chemical state present in the series of reactions, \( k_i \neq k_i(x_j), j = 1..n + 1 \), then depending on whether all \( k_i \) have an equal value or not, the system of differential equations will have the following exact solution:

- **unequal \( k_i \) and \( m \geq 1 \):**
  \[
  x_i(t) = \sum_{j=1}^{i} x_j(0) \left( \prod_{r=j}^{i-1} mk_r \right) \sum_{r=j}^{i} \frac{e^{-k_r t}}{\prod_{s=j \neq r} (k_s - k_r)}. \tag{44}
  \]

- **equal \( k_i \) and \( m \geq 1 \):**
  \[
  x_i(t) = \sum_{j=1}^{i} x_j(0) \frac{(mk)^{i-j} e^{-kt}}{(i-j)!}, \tag{45}
  
  x_{n+1}(t) = x_{n+1}(0) + \sum_{j=1}^{n} m^{n-j+1} x_j(0) \left( 1 - \sum_{s=0}^{n-j-1} \frac{(kt)^{n-j-s} e^{-kt}}{(n-j-s)!} \right). \tag{46}
  \]

### 5.1 The solution as a probability distribution

The distribution over the various chemical states present in the series of consecutive reactions can be described both by a number-averaged probability distribution and a weight-averaged distribution.

The number-averaged distribution is obtained by normalizing the distribution with the total number of 'particles' present:

\[
p_{N,i}(t) = x_i(t) \cdot \left[ \sum_{i=1}^{n+1} x_i(t) \right]^{-1}. \tag{47}
\]

The weight-averaged distribution is obtained by normalizing the distribution with the total amount of weight present in the system. To obtain such a distribution a weight must be assigned to each chemical state \( C_i \), let this weight be given by the operator \( a_i \). The weight-averaged probability distribution is then given by:

\[
p_{W,i}(t) = a_i x_i(t) \cdot \left[ \sum_{i=1}^{n+1} a_i x_i(t) \right]^{-1}. \tag{48}
\]

For the scission of nanotubes the length of the nanotube should be used as a weight operator. In the next paragraph it will be shown that the total length of nanotubes present at any moment is conserved for the solution to the set of differential equations.
5.2 The weight operator & conservation of mass

Intuitively one would expect the mass operator to be of the form $m^{1-i}$. It implies that the $m$ products (the two segments in which a nanotube will break) of a single reaction have a total mass equal to the mass of the reactant (the length of the initial nanotube). If the mass of each state is defined by this operator, then it can be shown that the total amount of mass, $s$, is conserved during the process.

$$\sum_{i=1}^{n+1} m^{1-i} x_i(t) = \sum_{i=1}^{n+1} m^{1-i} x_i(0) = s.$$  \hspace{1cm} (49)

For the process of nanotube scission the weight operator, which is taken to be the length of a nanotube, is indeed of the form $m^{1-i}$. The solution enforces that the total length of nanotubes in the system is conserved.

From here on the results presented are only valid for a consecutive process with a constant reaction rate. If the consecutive process is assumed to be sufficiently far from the end, it can be approximated as an infinite process. That is, the probability to find a particle in the final state, $C_{n+1}$, is negligible. For a process with a constant reaction rate and mass operator $a_i = m^{1-i}$, this leads to the following probability distributions:

$$p_{N,i}(t) = \sum_{j=1}^{i} p_{N,j}(0) \frac{(mkt)^{i-j} \exp^{-mkt}}{(i-j)!},$$  \hspace{1cm} (50)

$$p_{W,i}(t) = \sum_{j=1}^{i} p_{W,j}(0) \frac{(kt)^{i-j} \exp^{-kt}}{(i-j)!}.$$  \hspace{1cm} (51)

Note that the weight-averaged distribution is equal to the number-averaged distribution for $m=1$. Furthermore the weight-averaged distribution is independent of the number of product particles, $m$.

5.3 The expectation value of an observable

Let $b(t)$ be an observable and let $b_i$ be the value of the observable associated with the chemical state $C_i$. Then the expectation value of the observable $\langle b \rangle = b(t)$ can be calculated from both the number-averaged and weight-averaged probability distribution:

$$b_N(t) = \sum_{i=1}^{n+1} b_i p_{N,i}(t), \hspace{1cm} b_W(t) = \sum_{i=1}^{n+1} b_i p_{W,i}(t).$$  \hspace{1cm} (52)

Using these equations, the mean value, $\mu(t) = \langle i \rangle$, and standard deviation $\sigma(t) = \sqrt{\langle i^2 \rangle - \langle i \rangle^2}$ of the probability distributions as defined in equations (50, 51) can be determined:

$$\mu_N(t) = \mu_N(0) + mkt, \hspace{1cm} \sigma_N(t) = \sqrt{\sigma_N(0)^2 + mkt},$$  \hspace{1cm} (53)

$$\mu_W(t) = \mu_W(0) + kt, \hspace{1cm} \sigma_W(t) = \sqrt{\sigma_W(0)^2 + kt}.$$  \hspace{1cm} (54)
5.4 Dynamical Scale Invariance: I

In the introduction the results of Poulin et al. [1] were discussed. These results suggest that the decrease of the average nanotube length in time can be described by a power law. A power law is scale invariant. As the average length is determined by the nanotube length distribution one might wonder if the length distribution will display scale invariance.

The length distribution will be modeled as a consecutive process of first-order reactions in the next chapter. The question is then, do the solutions obtained at the beginning of this chapter display dynamical scale invariance? The concept of dynamical scale invariance in a series of consecutive first-order reactions with a constant reaction rate is explored in this section by first considering the solution for a monodisperse starting condition, which is a Poisson distribution. The results for a single Poisson distribution will be generalised to accommodate for polydisperse starting conditions, for which the solution is a linear combination of Poisson distributions with different mean values.

In paragraph 5.5 the possibility of scale invariance in the length distribution of nanotubes under sonication is investigated. In the analysis it is assumed that the distribution is scale invariant. The analysis presented is valid for a polydisperse starting condition and a reaction rate with a power-law dependence on the nanotube length, this includes a power law with an exponent of zero which results in a reaction rate independent of nanotube length.

5.4.1 Scale invariance in the Poisson distribution

Both the number-averaged, equation (50), and weight-averaged probability distribution, equation (51), for a series of consecutive reactions with constant reaction rate are a linear combination of Poisson distributions. A Poisson distribution gives the probability that a certain event occurs a number of $i$ times given that the expectation value of the number of events is a known quantity, $\mu$. If $k$ is the average time rate at which these events occur, then $\mu = kt$ and the Poisson distribution is given by the following equation:

$$p_i(t) = (kt)^i \exp(-kt)/i!.$$  \hspace{1cm} (55)

The expectation value, or average value, of $i$ is given by $\mu = kt$ and the standard deviation is given by $\sigma = \sqrt{kt}$. The variance is equal to the average value of the distribution, $\sigma^2 = \mu$.

The Poisson distribution & the central limit theorem

For a sufficiently large mean value, the Poisson distribution can be approximated by a normal distribution [25]. This is easily shown by applying the central limit theorem.

Consider two random variables $X_1$ and $X_2$ which are both Poisson distributed with an average value of $\mu_1$ and $\mu_2$ respectively. Then:

$$p(X_j = i) = \frac{\mu_j^i \exp(-\mu_j)}{i!}.$$  \hspace{1cm} (56)

Define the sum of these two Poisson variables as $Z = X_1 + X_2$. Then $p(Z = i)$ is given by:

$$p(Z = i) = \sum_{l=0}^{i} p(X_1 = i - l) \cdot p(X_2 = l).$$  \hspace{1cm} (57)
Substitution of equation (56) gives:

\[ p(Z = i) = \frac{\exp[-(\mu_1 + \mu_2)]}{i!} \sum_{l=0}^{i} \binom{i}{l} \mu_1^{i-l} \mu_2^l. \]  

(58)

The summation can be simplified by applying the binomial theorem:

\[ p(Z = i) = (\mu_1 + \mu_2)^i \exp[-(\mu_1 + \mu_2)]/i!. \]  

(59)

So \( Z \) is again Poisson distributed but now with an average and variance of \( \mu_Z = \mu_1 + \mu_2 \). As a result of this property, the distribution of a Poisson variable with an average value \( \mu \) is equal to the distribution of the sum of \( N \) independent Poisson variables, \( X_1, X_2, \ldots, X_N \) each with an average and variance of \( \mu/N \). The central limit theorem states that the sum of \( N \) independent and identically distributed random variables will approximately have a normal distribution. If the distribution from which each of these random variables is drawn has an average value \( \mu/N \) and variance \( \sigma^2/N \), then the normal distribution for the sum of these variables will have a mean \( \mu \) and a variance \( \sigma^2 \).

If the central limit theorem is applied to the Poisson distribution, it states that a Poisson distribution with mean value and variance of \( \mu \) can be approximated by a normal distribution with the same mean value and variance:

\[ p(X = i) = \frac{\mu^i \exp(-\mu)}{i!} \approx \frac{1}{\sqrt{2\pi \mu}} \exp\left(-\frac{(i - \mu)^2}{2\mu}\right). \]  

(60)

That a normal distribution with the same mean value and variance as the Poisson distribution is indeed an excellent approximation is shown in figure 16. In this figure a total of a 1000 points are shown. The x-coordinate of the \( i^{th} \) point is given by the value of \( i^{th} \) lowest value out of a total of a 1000 numbers randomly drawn from the normal distribution while the y-coordinate is given by the \( i^{th} \) lowest value of a 1000 numbers randomly drawn from the Poisson distribution.

![Figure 16: A Q-Q plot for a normal distribution and a Poisson distribution both with mean and variance equal to 2000. A total of 1000 numbers were randomly drawn from both distributions.](image)

If these points are on the line \( y = x \) then the two distributions are identical. In figure 16 the points clearly lie on the line \( y = x \), the normal distribution is an excellent approximation for the Poisson distribution. This type of plot is known as a Q-Q plot, here the plot was made
for a normal distribution and a Poisson distribution both with mean and variance equal to 2000.

If a normal distribution with mean and variance equal to the mean of the Poisson distribution, \( \mu \), is an excellent approximation for this Poisson distribution. Then the transformation as given by equation (61) should collapse Poisson distributions with different mean values onto a single, scale free, curve.

\[
p_j = \sqrt{\mu} \cdot p_i, \quad j = \frac{i - \mu}{\sqrt{\mu}}. \tag{61}
\]

Applying this transformation to a normal distribution with mean and variance equal to \( \mu \) transforms it to a normal distribution with mean equal to zero and a variance of one.

\[
p_i = \frac{1}{\sqrt{2\pi\mu}} \exp\left(-\frac{1}{2}\left(\frac{i - \mu}{\sqrt{\mu}}\right)^2\right) \rightarrow p_j = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}j^2\right). \tag{62}
\]

In figure 17 the Poisson distribution is plotted for various values of \( \mu \) in the left graph. In the right graph these distributions have been rescaled by (61), they collapse onto a normal distribution with a mean of zero and standard deviation of one which is represented by the solid blue line.

In conclusion, a Poisson distribution with a sufficiently high mean value can be rescaled to a normal distribution with a mean value of 0 and a variance of 1 by the transformation as given by (61).

**Limits to the validity of the normal approximation.**

The rescaling fails for a Poisson distribution with an insufficiently high mean value. Though the central limit theorem still holds, the Poisson distribution has no states with \( i < 0 \). As a result, a significant part of the low value tail of the normal distribution will not correspond to a value of \( i \geq 0 \) and thus not to the Poisson distribution. The approximation is poor for \( \mu = 2 \) as is shown in the left graph of figure 18. The lowest value \( j \) of a normal distribution \( p(j) \) which corresponds to the discrete state \( p_{i=0} \) of a Poisson distribution is given by \( j = -\sqrt{\mu} \). This value of \( j \) is obtained by applying the transformation as given by equation (61) to \( i = 0 \). The standard deviation of the scale free normal distribution is equal to one,
so the low value tail of the normal distribution is ‘occupied’ by Poisson states up to \(-\sqrt{\mu}\) times the standard deviation. Clearly the degree to which the low value tail of the normal distribution represents values of the discrete random variable, which has a Poissonian distribution, affects the quality of the approximation. For \(\mu \geq 9\) less than 0.1% of the normal distribution does not correspond to a part of the Poisson distribution.

![Figure 18](image)

**Figure 18:** On the left, the rescaled Poisson distribution for \(\mu = 2\) is shown. In the right graph the rescaled Poisson distribution for \(\mu = 9\) is shown. The blue dots correspond to the Poisson distribution while the red dots were obtained by applying a continuity correction to the normal distribution.

It is then reasonable to assume that a normal approximation is justified for a Poisson distribution with a mean value larger than 9, note that this is a rather arbitrary value though. In the right graph of figure 18 a rescaled Poisson distribution with an average value of \(\mu = 9\) is shown (the blue dots).

If the series of reactions has a finite length, the normal approximation will fail when the occupation of the final state becomes significant. A similar effect as what happens for small average values occurs at the high value tail of the normal approximation at this moment. The average of the distribution approaches the final state, there are no states which correspond to the high value tail of the normal distribution.

**A Continuity correction**

A Gaussian distribution is a continuous probability distribution whereas the Poisson distribution is discrete. To obtain a probability from a continuous distribution one needs to integrate the distribution over a certain area. A continuity correction assigns a part of the continuous probability distribution to each discrete value present in the discrete distribution [26]. The part of the continuous normal distribution corresponding to the discrete value \(i\) of a Poisson distribution is equal to the surface under the normal distribution between \(i - \Delta i/2\) and \(i + \Delta i/2\) where \(\Delta i\) is the interval between the following discrete values.

In the right graph of figure 18 the red points are the values obtained from the normal distribution after applying a continuity correction to it. The correction is very small, it however reduces the discrepancy between the approximate probability (given by the normal distribution) and the actual probability (the value of the Poisson distribution) somewhat. For a Poisson distribution with a high mean value, \(\mu\), and thus large variance the interval \(\Delta i\) is given by \(\Delta i = \mu^{-1/2}\). It becomes smaller as \(\mu\) increases, when it is sufficiently small a continuity correction is no longer required.
5.4.2 Scale Invariance in a consecutive first-order process

On the previous pages scale invariance for a consecutive process with a monodisperse starting condition was discussed. The central limit theorem allowed for a normal approximation of the distribution. The normal distribution is fully determined by just two numbers, the average and the variance of the distribution.

The solution for a polydisperse starting condition is a linear combination of Poisson distributions. Each of these Poisson distributions can be approximated by a normal distribution. Applying this approximation to equation (50, 51) gives:

\[ p_i(t) = \sum_{j=1}^{i} p_j(0) \frac{1}{\sqrt{2\pi\mu}} \exp \left[ -\frac{(i-(j+\mu))^2}{2\mu} \right]. \]  

(63)

Here \( \mu = mkt \) for the number-averaged distribution and \( \mu = kt \) for the weight-averaged distribution. Let \( j_{max} \) be the maximum value of \( j \) for which \( p_j(0) \neq 0 \). Then if \( \mu >> j_{max} \) the following is approximately true, \( \mu + 1 \approx \mu + j_{max} \approx \mu + \bar{j} \) and the distribution should be approximately equal to a single normal distribution with a mean \( \mu + \bar{j} \) and variance \( \mu + \bar{j} \):

\[ p_i(t) = \frac{1}{\sqrt{2\pi\mu}} \exp \left[ -\frac{(i-\bar{j}+\mu)^2}{2\mu} \right]. \]  

(64)

The approximation can be used because \( \mu \) increases in value as a function of time, see equations (53, 54). Essentially the approximation relies on the fact that after a sufficiently long time the system will be so far from its initial state that the initial state can be approximated as monodisperse, and as discussed earlier, a monodisperse system can be approximated by a normal distribution. Interestingly the mean value, \( \mu(t) \), and variance, \( \sigma^2(t) \), of the actual distribution are known. For an arbitrary, polydisperse, starting condition they are given by equations (53, 54). If these equations for the average and standard deviation of the distribution are used, then analogues to the monodisperse situation, the following transformation should rescale the discrete distribution as given by equations (50, 51) onto a time-independent normal distribution with a mean of 0 and a standard deviation of 1:

\[ p_j = \sigma(t) \cdot p_i, \quad j = \frac{i - \mu(t)}{\sigma(t)}. \]  

(65)

Below this scaling assumption is tested for three different starting condition, first a starting condition where two chemical states are present. Next a system which starts out with the first 10 states equally occupied. And last a system which starts out with a normal distribution as the initial state.

**Starting condition: Two states present**

Consider a system with \( p_1(0) = 0.5 \) and \( p_{10}(0) = 0.5 \). According to equations (53, 54) the expectation value and variance are given by:

\[ \mu(t) = 5.5 + \lambda, \quad \sigma(t) = \sqrt{20.25 + \lambda}. \]  

(66)

Here \( \lambda = mkt \) for the number-averaged expectation value of \( i \) while \( \lambda = kt \) for the weight-averaged expectation value.
In figure 19 the distribution for a system with this starting condition is shown for $t = 1$ (blue), $t = 15$ (red) and $t = 45$ (green). In the right graph the distribution has been rescaled by applying the transformation as given by (65). The rescaled distribution clearly evolves towards the predicted normal distribution, just as happened for a monodisperse system.

Figure 19: *On the left, the probability distribution for $t = 1, 15$ and $t = 45$ for a system with a starting configuration $p_1(0) = p_{10}(0) = 0.5$ is shown. In the right graph the corresponding rescaled distributions are shown.*

**Starting condition: First $n$ states present**
Consider a system which starts out with the first 10 states equally occupied, $p_1(0), p_2(0), ... p_{10}(0) = 1/10$. The distribution again evolves towards the proposed scale invariant normal distribution as is shown in figure 20.

Figure 20: *On the left, the probability distribution for $t = 1, 15$ and $t = 45$ for a system with the first 10 states equally occupied at $t = 0$ is shown. In the right graph the corresponding rescaled distributions are shown.*

**Starting condition: A normal distribution**
If the distribution starts out as a normal distribution it will have the shape of the scale invariant distribution at $t = 0$ and it should retain the shape of a normal distribution for all times. Calculations confirm that this is indeed the case, in figure 21 both the actual and rescaled distribution are shown for $t = 1, t = 15$ and $t = 45$. It was assumed that the distribution will become scale invariant when $\mu(t) >> j_{\text{max}}$. Clearly this is not necessary when the system has a normal distribution right from the start. This indicates that the degree to which the initial distribution resembles the scale invariant normal distribution has a strong influence.
on the amount of time required to reach the scale invariant distribution. An estimate for the amount of time required to reach the scale invariant distribution from a given starting distribution will not be discussed in this report.

\[ \begin{align*}
\frac{\partial \rho (L, t)}{\partial t} &= +mk (mL) \rho (mL, t) - k (L) \rho (L, t), \quad L > L_0, \\
\frac{\partial \rho (L, t)}{\partial t} &= +mk (mL) \rho (mL, t), \quad L_0/m \leq L < L_0.
\end{align*} \]

(67)

Here \( m \) is the number of pieces of equal length in which the nanotube breaks and \( \rho (L, t) \) is the number of nanotubes of length \( L \) at a time \( t \). For nanotubes shorter than \( L_0 \), as determined by equation (35), scission stops. The nanotube is too short to break.

In the scission process the total length, \( \phi \), of the nanotubes present at any moment is conserved:

\[ \int_0^\infty L \cdot \rho (L, t) \, dL = \phi. \]

(68)

It is assumed that the scission rate has a power-law dependence on the nanotube length:

\[ k (L) = kL^\alpha. \]

(69)

Let the average nanotube length be given by \( L(t) \). It is then assumed that the length distribution displays dynamical scale invariance and can be written as:

\[ \rho (L, t) = \frac{\phi}{\mathcal{L}^*(t)} f (L/L(t)). \]

(70)
Here \( f(x) \) is a scale free function which depends on a single parameter, \( x = L/\langle L \rangle \). Conservation of length implies that the expectation value of \( x \) is equal to one:

\[
\langle x \rangle = \int_0^\infty x f(x) dx = 1. \tag{71}
\]

Note that it is an assumption that the length distribution can be written as equation (70). This assumption is made because if the length distribution is of this form, the average length will decrease according to a power law under certain conditions as is shown below. In chapter 6 we will attempt to justify this assumption with simulation results. If the length distribution \( \rho(L,t) \) can be written as (70), then the distribution should collapse onto a single curve for various times by applying the following transformation:

\[
x = \frac{L}{\langle L \rangle(t)}, \quad f(x) = \frac{\langle L \rangle^2(t) \rho(L,t)}{\phi}. \tag{72}
\]

Substitution of equation (70) into the differential equations (67), multiplication by \( L/\langle L \rangle \), integration over the length and adding the results for each of the two differential equations gives the following equation:

\[
\frac{\dot{\langle L \rangle}(t)}{\langle L \rangle^{3+\alpha}(t)} = k \frac{(m - m^2)}{L_0^2} \cdot \frac{1}{f(L_0/\langle m\langle L \rangle(t) \rangle)} \int_{L_0/\langle L \rangle(t)}^\infty s^{\alpha+1} f(s) ds. \tag{73}
\]

Here \( s = m L/\langle L \rangle(t) \). Now a second assumption is made, the right-hand side of the previous equation is assumed to be independent of time. Again, we will not justify the assumption here, rather, we will attempt to justify the assumption with simulation results in the next chapter. If the right-hand side is indeed approximately independent of time, then dimensional analysis learns us that the equation can be written as:

\[
\frac{\dot{\langle L \rangle}(t)}{\langle L \rangle^{3+\alpha}(t)} = -\tau^{-1} \langle L \rangle^{-2-\alpha}(0). \tag{74}
\]

This differential equation is easily solved, the result is:

\[
\langle L \rangle(t) = \langle L \rangle(0) \left( 1 + \frac{(\alpha + 2) t}{\tau} \right)^{-1/(\alpha+2)}. \tag{75}
\]

For \( t << \tau \) the average length is asymptotically proportional to:

\[
\langle L \rangle(t) \propto \exp \left[ -t/\tau \right]. \tag{76}
\]

and for \( t >> \tau \) the average length is asymptotically proportional to:

\[
\langle L \rangle(t) \propto \left( \frac{\tau}{(\alpha + 2) t} \right)^{1/(\alpha+2)}. \tag{77}
\]

The exponential decay of the average length for early times, \( t << \tau \), derived here is in agreement with both the number-averaged length as determined from simulation and the average length as determined from the mathematics for a consecutive process. This will be
shown in chapter 6, there, the average length is derived from equation (52) and compared to simulation results. If the calculations presented here are correct then the characteristic time \( \tau \) introduced in the derivation is given by \( \tau = k^{-1} \).

For \( t \gg \tau \) the analysis results in a power-law dependence of the average nanotube length on time. This is the desired result! Even more encouraging is that substitution of \( \alpha = 3 \), as derived in paragraph 4.2.3 results in an exponent of \(-0.2\), consistent with the experimental results of Poulin et al. [1]

In the next chapter we will compare this to the results of simulations. Here it will be shown that though for a period of time the average length as determined from the simulation appears to decrease linearly on a double logarithmic plot, the slope is not constant for any period of time; there is an intermediate time interval during which the average length asymptotically approaches a power law. The simulations do not result in an exact power-law decay of the average length for any period of time.

For the period where the average length approximately decreases as a power law, the exponent of the power law was determined. The exponent of the power law as determined from the simulation is not in agreement with the exponent of \(-1/(\alpha + 2)\) as derived in this paragraph. The transformation as given by equation (72) does not result in a scale invariant distribution for any period of time. This suggests that not all of the assumptions made in the analysis in this paragraph are valid.

A more detailed discussion of the power-law behaviour of the average length as determined by simulations can be found in the next chapter. In future work we will take a closer look at the derivation presented in this paragraph and attempt to understand whether the assumptions made are valid or not.
6 Scission of carbon nanotubes under sonication

In chapter 4 the interaction between a single nanotube and a single bubble was thoroughly examined. A length-dependent scission rate was derived in paragraph 4.2.3. In chapter 5 the mathematics of a series of consecutive first-order reactions was discussed, the scission of carbon nanotubes under sonication can be described as such a process. The consecutive process of scission stops when the nanotubes reach a minimum length, the collapse of a bubble cannot exert a sufficiently high force on a nanotube of this length or shorter to cause the scission of it. This minimum length was derived in paragraph 4.3.

In this chapter all these elements are brought together to obtain a mathematical description of the length distribution as a function of time for nanotubes under sonication. The situation where the breaking rate is independent of the nanotube length will be considered for both a monodisperse and polydisperse starting distribution. In future work we will perform simulations for a length-dependent scission rate, in the last paragraph of this chapter the difficulties in simulating such a system are briefly discussed.

6.1 Simulation details

In chapter 5 the mathematics to describe a consecutive first-order process were discussed. To describe the sonication of carbon nanotubes in these terms, each state, \( C_i \), in the series of consecutive reactions should be considered as a carbon nanotube of length \( L_i \). If the carbon nanotube breaks into two equally sized pieces due to sonication, then the length of a nanotube segment after it has been broken a number of \( i \) times is:

\[
L_i = L_{n+1} \cdot 2^i 
\]

Here \( n \) is the number of times a carbon nanotube of the initial maximum length can break, \( L_{n+1} \) is the length of a carbon nanotube segment after it has broken in two a total of \( n \) times. The length \( L_{n+1} \) is determined by equation (35) and is of the order of 110 nm for the sonication of nanotubes in water at an acoustic power of 10 W and acoustic frequency of 20 kHz.

A system which initially has a monodisperse distribution was simulated, the results of this simulation are discussed in the next paragraph. The monodisperse system starts out with a total of 200 carbon nanotubes of length \( L_1 \). Nanotubes of this length can break a number of \( n = 19 \) consecutive times in the simulation. After 19 consecutive scissions of a nanotube of length \( L_1 \) the resulting nanotube segment will have a length of \( L_{20} \). Scission is no longer possible for a nanotube of this length, the simulation ends with a total of \( 200 \cdot 2^{19} \) carbon nanotubes of length \( L_{20} \).

The smallest length-scale in the simulation is given by \( L_{20} \), it is used as the unit of length in the simulation. For sonication in water this length is approximately 110 nm if a 10 W, 20 kHz acoustic field is applied. If this length is reached after 19 consecutive scissions, the initial nanotube length, \( L_1 \), is of the order of 6 cm. Though nanotubes with a length of multiple centimeters have been produced [28], the nanotubes that are sonicated are generally much shorter. Furthermore, it is a length well above the persistence length, which is of the order of 100 \( \mu \)m for a single-wall nanotube (see paragraph 2.2). Our scission model assumes that the nanotubes behave as rigid rod-like particles, the model is not valid for nanotubes with a length of the order of 6 cm. Nonetheless it is interesting to look at a long consecutive process in which the initial nanotubes are extremely long. Many of the results in chapter 5 are based
on the assumption that the process can be approximated as an infinite consecutive process. By allowing for a total of 19 consecutive scissions this assumption will be valid for the first part of the simulation in which the number of nanotubes with a length $L_{20}$ is still negligible.

For a simulation with an initial length distribution which is polydisperse the length of the nanotubes cannot be given by equation (78). The unit of length is again equal to the length of the shortest nanotube which can be obtained by sonication. In the simulation the maximum number of times a nanotube can break is given by $n_j$. Nanotubes with a length $1 \leq L < 2$ are obtained by the scission of the nanotubes with a length between $2 \leq L < 4$ and so on. In short, the nanotubes with a length between $2^{n_j-j-1} \leq L < 2^{n_j-j}$ are obtained by the scission of the nanotubes twice as long, $2^{n_j-j} \leq L < 2^{n_j-j+1}$. Each length interval $2^{n_j-j-1} \leq L < 2^{n_j-j}$ is divided into a discrete number of $n_i$ equally spaced lengths. The lengths present in the simulation are:

$$L_{i,j} = 2^{n_j-j} \cdot (2 - (i/n_i)) \cdot L_{n_i,n_j}.$$  

(79)

The unit of length is given by the shortest nanotube length in the simulation, it is equal to $L_{n_i,n_j}$. The scission of a nanotube of length $L_{i,j}$ results in two nanotubes with a length of $L_{i,j+1}$. Simulations were performed for $n_i = 20$ and $n_j = 4$, the maximum nanotube length present in the simulation is equal to 15.6 times the minimum length. The minimum length in the simulation is given by $L_{20,4}$, for sonication with a 10 W and 20 kHz acoustic field this is approximately 110 nm. The maximum length in the simulation is then approximately 1.7 \(\mu\)m, a length well below the persistence length. As a starting condition a normal distribution with an average length of $L_N(0) = 11.8$ and a standard deviation of $\sigma(0) = 1.6$ was used. The total number of nanotubes at $t = 0$ is 49681 each with a length between $L = 8$ and $L = 15.6$.

For a system with a length-independent scission rate, the scission rate determines the time scale of the simulation. The unit of time is given by the inverse of the scission rate, $k^{-1}$. If this unit of time is used, the scission rate is equal to 1 per unit time. In the simulation a timestep of $\Delta t$ is used, during this time interval each carbon nanotube has a probability $\Delta t$ to break. At each time step a random number, $p$, between 0 and 1 is generated for each nanotube present at that moment which is longer than the minimum length for which scission will still occur. If $p \leq \Delta t$ the carbon nanotube breaks into two pieces of equal length, if $p > \Delta t$ the nanotube does not break during the time step. In the simulation for a monodisperse initial distribution a total of 10,000 time steps of $\Delta t = 0.01$ were performed. In the simulation for a polydisperse initial distribution a total of 12,000 time steps of $\Delta t = 0.001$ were performed.

### 6.2 Results: monodisperse initial distribution

Assuming a monodisperse initial condition in which all carbon nanotubes have an initial length of $L_1$, the number-averaged distribution is given by equation (50):

$$L_i = L_{n+1} \cdot 2^{n+1-i}, \quad p_{N,i}(t) = \frac{(2kt)^{i-1} \exp(-2kt)}{(i-1)!}, \quad i = 1 \ldots n + 1.$$  

(80)

As long as the number of carbon nanotubes with length $L_{n+1}$ is negligible, the number averaged length, $\overline{L}_N(t)$, for an arbitrary polydisperse starting condition with an average length of $\overline{L}_N(0)$ at $t = 0$ can be derived from equation (52) and is given by:

$$\overline{L}_N(t) = \overline{L}_N(0) \exp(-kt).$$  

(81)
In paragraph 5.5 it was derived that the average length should initially decrease exponentially, this in agreement with the expression for the average length as derived above. In figure 22 it is shown that the average length as determined from the simulation initially also decreases exponentially.

The standard deviation, $\sigma_N(t)$, of the average length of the carbon nanotubes is given by:

$$\sigma_N(t) = \left[ \overline{L^2}_N(0) \exp(-3kt/2) - \overline{L}_N(0)^2 \exp (-2kt) \right]^{1/2}.$$  \hfill (82)

In figure 22 the number-averaged length as obtained from theory and simulation is plotted on the left. The unit of length in this plot is given by the average length at $t = 0$. The red line corresponds to the average length as predicted by equation (81) while the blue line correspond to the average length as determined from the simulation.

![Figure 22: The left graph shows the average length and the right graph the variance in length as determined from a number-averaged distribution. The red curves are theoretical predictions while the blue dots are the results of a Monte Carlo simulation.](image)

Initially theory and simulation agree, but for $t \approx 10$ the simulation starts to deviate from the theoretical prediction. This deviation appears because the number of carbon nanotube of length $L_{20}$ is no longer negligible, nanotubes of this length can no longer be broken. As a result the decrease in the average length as determined from simulation slows down as compared to the situation where all carbon nanotubes can still be broken. In the right graph the variance is divided by the square of the average length and is plotted as a function of time. For a monodisperse initial distribution $\overline{L^2}_N(0) = \overline{L}_N(0)^2$, and equation (82) can be simplified, dividing the simplified equation by the square of the average length gives:

$$\sigma_N(t)^2 / \overline{L}(t)^2 = \exp(-kt/2) - 1.$$  \hfill (83)

This equation is represented by the red curve in the right graph of figure 22 while the blue curve shows the results from the simulation. Simulation and theory are again in agreement for $t < 10$.

In paragraph 5.4 and 5.5 two approaches to determine possible scale invariance in the length distribution were discussed. The first approach suggests that the transformation as given by equation (65) should rescale the length distribution onto a single curve, a normal distribution with a mean value of 0 and variance of 1. This transformation is given by:

$$j = \frac{i - \mu}{\sigma}, \quad p_j = \sigma \cdot p_i.$$  \hfill (84)
Here $\mu = \langle i \rangle$ and $\sigma = \sqrt{\langle i^2 \rangle - \langle i \rangle^2}$ are the mean value and standard deviation of $i$. The value of $i$ in terms of the nanotube length as given by equation (80) is:

$$i = n + 1 - [\log (L_i) - \log (L_{n+1})] / \log (2).$$

(85)

The transformation given by equation (84) can now be written in terms of the nanotube length $L_i$:

$$j = \frac{\langle \log (L_i) \rangle - \log (L_i)}{\sqrt{\langle \log (L_i^2) \rangle - \langle \log (L_i) \rangle^2}}, \quad p_j = \frac{\log (2)}{\sqrt{\langle \log (L_i^2) \rangle - \langle \log (L_i) \rangle^2}} \cdot p_i. \quad (86)$$

In figure 23 the actual length distribution is shown on the left while the rescaled distribution is shown on the right.

![Graph showing length distribution](image)

Figure 23: The length distribution for $t = 2$ (blue squares), $t = 6$ (green circles) and $t = 10$ (red triangles). On the left the actual distribution is shown, open symbols correspond to simulation results, closed symbols to theoretic predictions. On the right the rescaled distribution is shown.

In the left graph the closed symbols correspond to the theoretical prediction as given by equation (80), the open symbols correspond to the simulation results. The blue curve in the right graph is a normal distribution with a mean value of 0 and a variance of 1, the closed symbols correspond to the results of the simulation.

For $t = 2$ (blue) the left graph shows that the length distribution predicted by theory is in reasonable agreement with simulation results. The number of nanotube segments in the system is still low at this moment, there are just 1500 nanotube segments. As a result statistics are limited and there are deviations between theory and simulation. The right graph shows that the rescaling works fairly well, the probabilities of the discrete distribution are approximately equal to the probabilities as given by the normal distribution.

For $t = 6$ (green) the left graph shows that the theoretical prediction for the length distribution is in near perfect agreement with simulation results, the open symbols which correspond to the simulation results are hidden under the closed symbols which correspond to the theoretical prediction. The statistics are now a lot better, there are a total of 82,000 nanotube segments in the system at this moment. The right graph shows that the rescaling again works fairly well, note that the high-value tail of the normal distribution is not ‘occupied’.

49
For $t = 10$ (red) this effect is even stronger, the right graph shows that the normal approximation no longer works. That this would happen was already predicted in paragraph 5.4.1. It is the result of the finite length of the scission process. Many nanotube segments have reached the terminal length of $L_{20} = 1$ as can be seen from the left graph. At the same time the standard deviation of the length distribution is very large as can be seen from figure 22. The high-value tail of the normal distribution then corresponds to nanotubes much longer than the average length (see equation (84)), from the left graph it is clear that there are no very long nanotubes ($L > 1000 \cdot L_{20}$) in the system, they have all been broken into shorter segments. As a result the high-value tail is not occupied and the normal approximation is no longer valid. In the left graph, theory and simulation results deviate for a different reason. The theoretical prediction for the length distribution is based on the assumption that the consecutive scission process is infinite. This approximation is no longer valid for $t > 10$, there are many nanotube segments of the terminal length $L_{20}$ which can no longer break. As a result theory and simulation are and should not be in agreement.

The second approach to scale invariance, as introduced in paragraph 5.5, suggests that the average length decreases as a power law with an exponent of $-0.5$ for a length independent scission rate for sufficiently large times. In figure 24 the average length is shown in a double logarithmic plot, in the right graph the slope of this plot is shown.

![Figure 24](image)

**Figure 24:** The average length is shown in a log-log plot on the left, on the right the slope of this plot is shown as a function of time.

There appears to be a region where the average length shows a linear decrease in the double logarithmic plot. The slope here is however approximately equal to $-6.5$, much larger than the value of $-0.5$ which was predicted in paragraph 5.5. The right graph shows that the slope is not constant in this region. It passes through a minimum, because of this it is approximately constant for a small period of time and the slope appears to be constant in the left plot. The power-law behaviour appears in an intermediate asymptotic way. The time period for which the power-law behaviour is observed in the simulation is less than a decade of time, this is in disagreement with the experimental results of Poulin et al. [1], where a power-law decay over three decades of time was observed. In conclusion, the average length as determined from simulation does not show a real power-law decay for any period of time, at least not for a constant scission rate. The observed slope is not in agreement with theory or simulation and the time period for which it is observed is not in agreement with experiment.

That the average length should decrease as a power law was derived by assuming that the
length distribution is scale invariant and of a specific mathematical form as given by equation (70). It has been checked whether the length distribution as obtained from the simulation is of this form, this is not the case. These results suggest that the assumptions made in the analysis in paragraph 5.5 cannot be valid, in future work we will attempt to understand why the power-law behaviour as derived in paragraph 5.5 is not in agreement with the results of the simulation.

In figure 25 the average length and standard deviation as determined from a weight-averaged distribution are shown.

![Figure 25: The left graph shows the average length and the right graph the variance in length as determined from a weight-averaged distribution. The red curves are theoretical predictions while the blue dots are the results of a Monte Carlo simulation.](image)

To obtain the weight-averaged, or more precisely the length-averaged, distribution \( L_i = L_{n+1} \cdot 2^{n+1-i} \) should be used for \( a_i \) in equation (48). The weight of a state is now equal to the length of the carbon nanotube corresponding to the state. If it is again assumed that the process is sufficiently far from the final state, the weight-averaged distribution is given by equation (51):

\[
L_i = L_{n+1} \cdot 2^{n+1-i}, \quad p_W(i, t) = \frac{(kt)^{i-1} \exp(-kt)}{(i-1)!}, \quad i = 1...n+1. \tag{87}
\]

Again, assuming that the number of carbon nanotubes with length \( L_{n+1} \) is negligible, the weight-averaged length for any polydisperse starting condition is given by:

\[
\bar{L}_W(t) = \bar{L}_W(0) \exp(-kt/2). \tag{88}
\]

And the standard deviation of the length distribution is given by:

\[
\sigma_W(t) = \left[ \bar{L}_W^2(0) \exp(-3kt/4) - \bar{L}_W(0)^2 \exp(-kt) \right]^{1/2}. \tag{89}
\]

In figure 25 the average length and variance as determined from the weight-averaged distribution are plotted in the same manner as they were plotted for the number-averaged distribution. Deviations between theory and simulation now start to appear at \( t \approx 25 \). The deviations appear at a later moment as compared to the number-averaged case. This is easily understood as the weight assigned to a carbon nanotube is equal to its length. The shortest carbon nanotubes, which can no longer break, have the lowest possible weight and thus their influence on the average length is reduced as compared to the number-averaged situation. It are the shortest nanotubes that cause the deviation between theory and simulation, this deviation thus appear at a later moment.
6.3 Results: polydisperse initial distribution

A monodisperse initial distribution is not very realistic, in reality there will be nanotubes of different lengths present at $t = 0$. The length distribution is continuous, there will be more than only a select number of lengths present in the system. This is somewhat problematic as the mathematics derived in chapter 5 are suited to a process with a discrete number of lengths rather than a process with a continuum of lengths present. The linearity of the scission process in combination with a constant, length independent, scission rate however allows us to reduce the polydisperse starting condition to a limited sum of monodisperse starting conditions. The evolution of the monodisperse starting condition can again be described by the mathematics of chapter 5 and the solution for the polydisperse starting condition is simply the sum of the solutions for each of the monodisperse starting conditions. How this approach to a polydisperse starting condition works is discussed in this paragraph.

The length distribution at the start of the simulation is shown on the left in figure 26. There are only nanotubes with a length between $L = 8$ and $L = 16$, each scission of a nanotube within this length range results in two nanotubes within the length range of $L = 4$ up to $L = 8$. The scission rate is constant, the number of scissions of nanotubes of a certain length is proportional to the number of nanotubes with this length. As a result the shape of the distribution between $L = 8$ and $l = 16$ is retained during the scission process. In the length range of $L = 8$ to $L = 4$ a length distribution with the same shape as the initial distribution but with half the width will appear, the scission of these nanotubes results in a length distribution with the same shape, but now with a quarter of the width as the initial distribution, between $L = 4$ and $L = 2$ and so on.

Figure 26: The left graph shows the length distribution as obtained from simulation at $t = 0$, the right graph shows the length distribution at $t = 1$.

The right graph in figure 26 shows the length distribution at $t = 1$ as determined from the simulation. Here the ‘copies’ of the initial distribution are clearly visible. If the initial distribution, which is restricted to a length of $8 \leq L < 16$ has an average length of $\bar{L}(0)$, then the average length of the nanotubes with a length of $L = 8$ up to $L = 16$ will always be equal to $\bar{L}(0)$ as the shape of the distribution is retained. What changes is the amplitude of this distribution.

As the length distribution for $4 \leq L < 8$ is equal in shape, the average length of the nanotubes with a length in this range will be equal to $\bar{L}(0)/2$ at all times, and so on. Again, it is the amplitude of the distribution which changes over time. If this amplitude is given by
$x_i(t)$, then the full length distribution can be described by:

<table>
<thead>
<tr>
<th>$i$</th>
<th>Length range</th>
<th>Average length</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$8 \leq L &lt; 16$</td>
<td>$L(0)$</td>
<td>$x_1(t)$</td>
</tr>
<tr>
<td>2</td>
<td>$4 \leq L &lt; 8$</td>
<td>$L(0)/2$</td>
<td>$x_2(t)$</td>
</tr>
<tr>
<td>3</td>
<td>$2 \leq L &lt; 4$</td>
<td>$L(0)/4$</td>
<td>$x_3(t)$</td>
</tr>
<tr>
<td>4</td>
<td>$1 \leq L &lt; 2$</td>
<td>$L(0)/8$</td>
<td>$x_4(t)$</td>
</tr>
</tbody>
</table>

The amplitude $x_i(t)$ is simply the number of nanotubes in the corresponding length range. The polydisperse problem is now reduced to the scission of $x_i(t)$ nanotubes with a length of $L_i = L(0) \cdot 2^{1-i}$. The amplitude $x_i(t)$ is given by equations (45, 46), here $n = 3$ and $x_1(0) = 1, x_2(0) = x_3(0) = x_4(0) = 0$.

The number-averaged length at a time $t$ can now be determined mathematically:

$$L(t) = \frac{\sum_{i=1}^{4} 2^{1-i} L(0) \cdot x_i(t)}{\sum_{i=1}^{4} x_i(t)}.$$

Note that this is not an approximation, it is an exact expression for the average length. In figure 27 the average length as determined from this equation is represented by the red curve. It is in perfect agreement with the average length as determined from simulation which is represented by the blue dots.

![Figure 27](image-url)

**Figure 27:** The graph shows the number-averaged average length as a function of time. The red curves show the theoretic predictions as given by equation (90), the green curve shows the theoretic prediction as given by equation (81). The blue dots are the results obtained from the simulation.

When the initial length distribution is not restricted to nanotubes with a length between $L = 8$ and $L = 16$ but there are for example also nanotubes with a length between $L = 4$ and $L = 8$ present at $t = 0$, then the system can be split into two systems. One with an initial distribution with nanotubes with a length between $L = 4$ and $L = 8$ and one with an initial distribution with the nanotubes with a length between $L = 8$ and $L = 16$. The average length as a function of time can again be determined in the same way as above for each subsystem. Because the scission process is linear the solution for the entire initial length distribution is simply the weighted sum of the two solutions as determined for the two subsystems.

For a monodisperse starting condition the average length was approximated by equation
In principle it is still valid, the scission process is linear. However, in deriving this equation it was assumed that the scission process can be approximated as an infinite process. This is not a good approximation as the consecutive process consists of just 4 ‘states’. This approximation is represented by the green line in figure 27 and indeed only for the first few moments the approximation works.

Figure 28: The average length is shown in a log-log plot on the left, on the right the slope of this plot is shown as a function of time.

In figure 28 the average length is shown in a double logarithmic plot on the left while the right graph shows the slope of this graph. Between $t = 1$ and $t = 3$ the slope is again more or less constant at a value of $-0.8$. Again the power-law behaviour appears in an intermediate asymptotic way and the time interval over which it is observed is again far shorter as observed in experiments [1]. The slope is significantly different from the one obtained in the simulation for a monodisperse starting condition, there a slope of approximately $-6.5$ was observed. In paragraph 5.5 a slope of $-0.5$ was predicted for a system with a constant scission rate, the calculations made there do not explain why the slope for a monodisperse system with a maximum of 19 consecutive scissions is different from the slope as observed here for a polydisperse system with a total of 4 consecutive scissions. The maximum number of scissions and the initial distribution are the only differences between the simulations for a monodisperse initial distribution and the simulation for a polydisperse initial distribution. In conclusion either of these factors could affect the exponent of the observed power law. What seems most likely is that the ratio between the maximum nanotube length initially present and the minimum length which can be obtained by sonication, that is the maximum number of scissions, determines the exponent of the observed power law. In future work we will attempt to confirm this through simulations and gain an understanding of what determines the observed slope and the exponent of the corresponding power law.

### 6.4 A length-dependent scission rate

The situation where the scission rate depends on the length of a nanotube is in many ways more complicated than the situation where the scission rate is constant. The time scale at which scission occurs is no longer constant. This is problematic for the simulation because it implies a wide range of time scales at which processes occur. The size of a time step should be suited to the fastest scission rate in the simulation. As a result the simulation will be very inefficient for the slower processes. In paragraph 4.2.3 it was shown that the scission rate for a fictitious nanotube (the tensile strength was assumed to be far smaller than the
actual tensile strength of a nanotube) is proportional to $L^3$, the time scale at which scission takes place thus strongly depend on the nanotube length. In future work we will nonetheless attempt to simulate a system with a non-constant scission rate and attempt to model the length distribution in a similar manner as was done for a process with a constant scission rate in the previous paragraph. The mathematical expression, equation (44), for a consecutive process with a non-constant reaction rate might prove to be useful in this attempt.
7 Technology Assessment

Carbon nanotubes have many unique properties and potential applications. In this chapter we will focus on just one industrial application of carbon nanotubes. This application is based on the electric conductivity of a carbon nanotube. For certain classes of nanotubes, theoretical predictions of their conductivity result in a conductivity which is three orders of magnitude greater than the conductivity of copper. By dispersing nanotubes in a bulk material a percolating network of nanotubes can be formed, this percolating network greatly enhances the conductivity of the host material, the percolation threshold depends on the length of the nanotubes used and decreases with increasing nanotube length [2].

Though the nanotubes are black, a thin flexible, transparent and conductive layer can be obtained by dispersing a relatively small number of nanotubes in a thin layer. The nanotubes in this thin layer form a percolating network. A transparent and conductive, though not necessarily flexible, material is required for the production of any solar cell or touch screen. With the introduction of products as the iPhone and iPad, touch screen technology has become widely used. Currently thin layers of indium tin oxide are being used in industry when a conductive transparent layer is required. It is however an expensive material, the natural reserves of indium are almost depleted and the production of these layers requires expensive vacuum technology. Thin films of conducting carbon nanotube networks are seen as a replacement of indium tin oxide in the near future. The nanotube layer will be both cheaper and easier to produce and far less brittle than indium tin oxide. The lifetime of the device should as a result be longer.

The transparent and conductive nanotube layers are produced by spraying a dispersion of nanotubes on a suitable substrate. In order to obtain this nanotube dispersion, bundles and ropes of nanotubes are sonicated until a dispersion of individual nanotubes is obtained. The amount of nanotubes required to obtain a percolating network depends on the length of the nanotubes used to create this network. The longer the nanotubes the less nanotubes are required [2]. Perhaps even more importantly, the less nanotubes are required to obtain a percolating network, the higher the transparency of the thin layer. As a result it is beneficial if the nanotubes are still as long as possible after sonication. Through understanding of the scission process of nanotubes under sonication it will be possible to minimise the decrease in average length during sonication while a dispersion of nanotubes is still obtained. In this way the transparency of the conductive nanotube layers can be maximised and the production costs for these layers can be minimised.
8 Summary & Outlook

The aim of our work was to construct a theoretical model which would explain the evolution of the length distribution of carbon nanotubes under sonication. In this report the basis of this model is presented. Though the first results are encouraging there remains quite some work to be done before an attempt can be made to compare our model to actual experiments on the sonication of carbon nanotubes. Here the important results and assumption are discussed per chapter and the parts of our model which require more work are listed.

In chapter 2 the properties of a carbon nanotube were discussed. In our model we assume that a carbon nanotube can be approximated as a rigid rod-like particle, it was shown that this is a reasonable assumption for nanotubes shorter than 100 µm, the persistence length of a single-wall nanotube. Scission of a nanotube occurs when the tensile strength of the nanotube is overcome by an external force. Theoretical predictions for the tensile strength are of the order of 100 GPa. When the tensile strength is determined experimentally a tensile strength of the order of 10 GPa is found, this deviation from theory can partly be explained by the presence of defects in a nanotube. We assume that defects can locally lower the tensile strength of a nanotube. In our current model all nanotubes have an equal diameter and tensile strength, in reality this will not be the case. A dispersion of nanotubes will consist of nanotubes with varying diameter, chiral vector and tensile strength. Our current model indicates that a difference in diameter and tensile strength will only be of influence on the minimum length which can obtained through sonication.

In chapter 3 the transient collapse of a bubble was modeled by Lord Rayleigh’s model for the collapse of an empty cavity. This model is a simple approximation for the process of transient cavitation. Nonetheless, the model gives a full description of the fluid flow following the collapse of a bubble. Based on this model the interaction between a bubble and nanotube was investigated in chapter 4. Here it quickly became clear that the approximation of transient cavitation by Rayleigh’s model for the collapse of an empty cavity is too simplistic to explain the scission of a nanotube. In future work the same analysis of the interaction between a bubble and nanotube as presented in chapter 4 will be made but now based on the Rayleigh-Plesset equation for the dynamics of a bubble in an acoustic field. If it proves to be necessary we will look into the final stages of collapse where the collapse is supersonic.

As mentioned, in chapter 4 the interaction between a nanotube and a bubble was discussed. Using the model as published by Terentjev et al. [23], it was shown that scission will occur at the middle of the nanotube as long as the nanotube is sufficiently long. For sonication in water, the minimum length for which scission will still occur is of the order of 200 nm. We determined the actual position of a nanotube during the collapse of a bubble as a function of time and determined the stress exerted on the nanotube based on this position. It was shown that there exists a maximum initial distance between the nanotube and the bubble for which scission will still occur, this distance depends on the length of the nanotube. Based on this maximum initial distance a length-dependent scission rate was derived, the scission rate is proportional to the third power of the nanotube length. Note that two approximations were made in deriving this scission rate. First of all, we considered a fictitious nanotubes with a far smaller tensile strength than the actual tensile strength of a nanotube. Second we determined the maximum stress at a somewhat arbitrary moment. As mentioned, in future work we will repeat the analysis without resorting to these approximations and use
the Rayleigh-Plesset equation to model the dynamics of transient cavitation.

Finally it was shown that the presence of defects will result in non-midtube scission and how this can lead to the slowing down of the scission process. In future work a more advanced statistical model will be made to obtain a more thorough understanding of the role of defects. As a last remark, the friction between a nanotube and the surrounding liquid was assumed to be approximately independent of the nanotube diameter. The validity of this approximation was not discussed in any detail in this report but is something which should be looked into in our future work.

In chapter 5 the mathematics of a series of consecutive first-order processes was discussed. A set of differential equation was introduced and an exact solution to these differential equations was obtained. It was shown that the solution for a constant scission rate can be approximated by a linear combination of Poisson distributions. Through application of the central limit theorem it was shown that this linear combination of Poisson distributions can be approximated by a normal distribution with the same mean and variance as the actual distribution. Based on this property a transformation was introduced which rescales the distribution over the consecutive states onto a normal distribution with a mean value of zero and variance of one. This rescaling only works if the process is sufficiently long, for the scission of nanotubes this is not necessarily the case.

In the final paragraph of this chapter it was assumed that the length distribution displays scale invariance and is of a specific mathematical form. Based on this assumption it was shown that the average length should decrease as a power law for sufficiently large times. Though the average length as obtained from simulations seems to decrease as a power law for a period of time, it was shown in chapter 6 that this power-law behaviour is only observed as intermediate asymptotic behaviour. Here it was also shown that the exponent of the power-law approximation for the results of our simulation is not in agreement with theory or experiment. Furthermore, it was also shown that the time interval over which power-law behaviour is observed in the simulation is not in agreement with experiment. Currently we do not fully understand why the power-law decay as derived in paragraph 5.5 is not in agreement with simulation results. In future work we will attempt to understand this deviation between theory and simulation.

In chapter 6 the scission process was simulated by a Monte Carlo simulation. In the simulation there is a minimum length for which scission will still occur and scission occurs right at the middle of the nanotube. Simulations for a constant scission rate were performed, both for a monodisperse and polydisperse starting condition. The mathematics as derived in chapter 5 were compared to the results of the simulations. It was shown that the mathematics as derived in chapter 5 describe the simulation results very well. In future work more simulations will be carried out, including for systems with a length-dependent scission rate. We will attempt to describe the results of these simulations with the mathematics as introduced in chapter 5. Finally we hope to apply our model to the results of actual experiments on the sonication of carbon nanotubes and compare the results.
Acknowledgements

A thesis might be written by a single person, the work that is presented in it is hardly ever the product of a single person. As a result I would like to acknowledge the contributions that others have made to this report.

Firstly, I would like to thank Paul van der Schoot, my supervisor. Your supervision has been of tremendous help in writing this thesis. Your advice and guidance has been both critical and enthusiastic (to say the least!). It has helped me appreciate the little day-by-day progress that I made. During the final stages of this project, you forced me to deliver a thesis better written than any of my previous work. With your advice and tips, I feel that I have not only achieved this, but learned a lot about doing research and writing a scientific report in the process. Your enthusiasm, excellent supervision and attention to my development as a scientist made it easy to accept your offer for a PhD position under your supervision. I look forward to the coming four years and hope to continue to experience your enthusiasm and valuable advice!

Secondly, I would like to thank the members of my graduation committee, Richard Engel, Thijs Michels and Alexey Lyulin, for reading my report and taking the time to discuss my work with me. Most of the tips and advice that I received during this discussion have been incorporated in this final version of my thesis. The rest of the advice will prove to be valuable as I will continue to work on the scission of nanotubes under sonication.

In the final place, I’d like to thank the members of our group for providing a pleasant working environment!

Joris
A Derivation of Blake Threshold.

Assume there is a bubble with radius $R_0$ within a liquid. The internal pressure in the bubble is the sum of the Laplace pressure and the external liquid pressure. Neglecting hydrostatic effects, the liquid pressure can be approximate by the atmospheric pressure, $p_0$. Assume isothermal conditions, then, if the gas behaves as an ideal gas, $pV$ is constant. For the initial bubble with radius $R_0$, $pV$ is given by:

$$\left( p_0 + \frac{2\sigma}{R_0} \right) \frac{4}{3} \pi R_0^3. \quad (91)$$

If the external pressure is lowered by an amount of $p_A$, then the volume of the bubble will have to change to keep $pV$ at a constant value. The bubble has to change its radius to $R$ in response to the change in external pressure, $R$ is determined by:

$$\left( p_0 - p_A + \frac{2\sigma}{R} \right) \frac{4}{3} \pi R^3 = \left( p_0 + \frac{2\sigma}{R_0} \right) \frac{4}{3} \pi R_0^3. \quad (92)$$

From this equality the value of $p_A$ required to obtain a bubble radius $R$ can be determined:

$$p_A = p_0 - \left( p_0 + \frac{2\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^3 + \frac{2\sigma}{R}. \quad (93)$$

In figure 29, equation (93) is plotted for a bubble in water under ambient conditions with an initial radius of 0.2 $\mu$m.

Figure 29: On the left, a plot of the acoustic pressure required to reach a bubble with radius $R$ as given by equation (93) is shown, the region beyond the maximum corresponds to unstable growth. On the right a plot of equation (96) is shown.

As the radius of the bubble increases the “confining effect” of the Laplace pressure decreases. To keep $pV$ constant the bubble will have to increase in size even further, which results in an even further decrease of the Laplace pressure. The bubble has become unstable and will grow explosively.

There is a critical radius at which the Laplace pressure can no longer contain the growth of the bubble, this radius is given by $\frac{\partial p_A}{\partial R} = 0$. Solving this equation for $R$ gives:

$$R_B = \sqrt[3]{\frac{3R_0^3}{2\sigma} \left( p_0 + \frac{2\sigma}{R_0} \right)} \cdot \quad (94)$$
Substitution of $R_B$ in equation (93) gives the Blake threshold:

$$p_B = p_0 + \frac{8\sigma}{9} \sqrt{\frac{3\sigma}{2R_B^3 (p_0 + 2\sigma/R_B)}}.$$  

This equation can be rewritten in dimensionless form:

$$\frac{p_B}{p_0} = 1 + \frac{1}{\frac{4}{27} (p_0/p_\xi)^3 + (p_0/p_\xi)^2}, \quad p_\xi = \frac{2\sigma}{R_0 \sqrt{3(1 + (p_0R_0)/(2\sigma))}}.$$  

A plot of $p_B/p_0$ as a function of $p_0/p_\xi$ is shown in the right graph in figure 29.

### B Derivation of the maximum bubble radius

Let the acoustic field be given by:

$$P(t) = -p_A \sin(\omega t).$$  

If the Laplace pressure is neglected and the pressure in the bubble is taken to be equal to zero (Rayleigh considered the collapse of an empty cavity), the pressure difference between the inside of the bubble and the external liquid pressure is equal to:

$$\Delta P = p_A \sin(\omega t) - p_0.$$  

The bubble expands during the time that $\Delta P$ is positive. This period begins and ends with the two times, $t_1$, $t_2$ for which $\Delta P = 0$. Approximate $\Delta P$ by a second order Taylor expansion around $\omega t = \pi/2$. Determine $t_{1,2}$ for which the second order expansion is zero:

$$t_{1,2} = \frac{1}{\omega} \left[ \frac{\pi}{2} \pm \sqrt{2 \left( 1 - \frac{p_0}{p_A} \right)} \right].$$  

The time during which the pressure outside the bubble is lower than the internal bubble pressure is then given by:

$$t_m = t_2 - t_1 = \frac{2}{\omega} \sqrt{2 \left( 1 - \frac{p_0}{p_A} \right)}.$$  

During this time the average pressure can be approximated by:

$$\overline{\Delta P} = \frac{1}{t_m} \int_{t_1}^{t_2} (p_A \sin(\omega t) - p_0) \, dt \approx \frac{2}{3} (p_A - p_0).$$  

To obtain this approximation $\Delta P$ was again approximated by a second order Taylor expansion around $\omega t = \pi/2$. The average wall velocity can be obtained from the Rayleigh model which is derived in paragraph 3.3.3. The wall velocity is given by equation (12), where in this case $R_{\max}$ must be replaced by the initial bubble radius, $R_0$. As $R \geq R_0$ the wall velocity will quickly approach $v = (2\overline{\Delta P}/3\rho)^{1/2}$. This velocity can be used as the average wall velocity, the maximum radius, $R_1$, obtained at $t_2$ can then be approximated by:

$$R_1 = vt_m = \frac{4}{3\omega} (p_A - p_0) \sqrt{\frac{2}{p_A \rho}}.$$  

61
At $t = t_2$ the pressure between the interior and exterior of the bubble is zero and for $t > t_2$ the exterior pressure becomes greater and starts to compress the bubble. At this moment the radial flow has a kinetic energy equal to:

$$\frac{1}{2}mv^2 = \frac{4\pi \Delta P}{3} R_i^3. \quad (103)$$

This equation for the kinetic energy is obtained by substitution of $\dot{R} = (2\Delta P/3\rho)^{1/2}$ in the equation for the kinetic energy of an incompressible fluid flow following the collapse of a bubble, which is given by $2\pi \rho R^3 \dot{R}^2$ and which was derived in paragraph 3.3.3. The final step in the derivation is to assume that this kinetic energy is used to expand the bubble to its maximum radius, $R_{\text{max}}$:

$$\frac{1}{2}mv^2 = p_0 \left( \frac{4}{3} \pi R_{\text{max}}^3 - \frac{4}{3} \pi R_i^3 \right). \quad (104)$$

From this equation an expression for $R_{\text{max}}$ is easily obtained:

$$R_{\text{max}} = \frac{4}{3\omega} \left( p_A - p_0 \right) \sqrt{\frac{2}{p_A \rho} \left[ 1 + \frac{2(p_A - p_0)}{3p_0} \right]^{1/3}}. \quad (105)$$

This equation can be rewritten in dimensionless form:

$$R_{\text{max}}/R_\xi = \left( 1 - \frac{p_0}{p_A} \right) \left( \frac{1}{3} + \frac{2}{3} \frac{p_A}{p_0} \right)^{1/3}, \quad R_\xi = \frac{4}{3\omega} \sqrt{\frac{2p_A}{\rho}}. \quad (106)$$

$R_{\text{max}}/R_\xi$ is plotted as a function of $p_A/p_0$ in figure 30.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure30.png}
\caption{A plot of $R_{\text{max}}/R_\xi$ as a function of $p_A/p_0$.}
\end{figure}

C Wall position and velocity as a function of time

The bubble radius, $R$ changes in time during the collapse of the bubble. In Rayleigh’s model for the collapse of an empty cavity, this radius obeys the following differential equation:

$$\dot{R} = v(R) = -\sqrt{\frac{2}{3\rho} \left( \frac{R_{\text{max}}^3}{R^3} - 1 \right)}. \quad (107)$$
Separation of variables gives:

\[-\sqrt{\frac{2p}{3\rho}} \int_0^t \, dt' = -\sqrt{\frac{2p}{3\rho}} t = \int_{R_{\text{max}}}^R \sqrt{\frac{R_{\text{max}}^3}{R^3} - 1} \, dR'.\]  \hspace{1cm} (108)

The right hand side of this equation was integrated numerically in Mathematica for:

\[R\[i] = R_{\text{max}} - i \frac{R_{\text{max}}}{10^5}, \quad i = 1...99.999.\]  \hspace{1cm} (109)

With the numeric approximation for the right hand side of equation (108), the time at which the bubble has a radius \(R\[i]\) can be solved.

With the time at which the bubble has a radius \(R\[i]\) known, the velocity of the bubble wall at \(t = t\[i]\) is given by equation (12):

\[v(R, t\[i]) = -\sqrt{\frac{2p}{3\rho} \left( \frac{R_{\text{max}}^3}{R\[i]^3} - 1 \right)}.\]  \hspace{1cm} (110)

**D \hspace{1cm} Nanotube velocity**

The velocity of a nanotube is given by equation (17) where \(v(r)\) is given by equation (21). The velocity of the nanotube is then given by:

\[v_{\text{cnt}} = \dot{r}_c = -\frac{R^2}{r_c (r_c + L)} \sqrt{\frac{2p}{3\rho} \left( \frac{R_{\text{max}}^3}{R^3} - 1 \right)}.\]  \hspace{1cm} (111)

In appendix C the bubble radius, \(R\[i]\), was determined as a function of time, \(t\[i]\). Denote the position of the leading edge of the nanotubes at time \(t\[i]\) as \(r_c[i]\) and the initial position as \(r_c[0]\). Using this position for the nanotube, its velocity, \(\dot{r}_c[1]\), is determined for the radial inward flow at \(t[1]\) as given by equation (110). The average velocity between \(t[0]\) and \(t[1]\) is approximated by \((\dot{r}_c[0] + \dot{r}_c[1]) / 2\). Finally the position of the nanotube at \(t[1]\), \(r_c[1]\), is approximated by:

\[r_c[1] = r_c[0] + (t[i] - t[i - 1]) (\dot{r}_c[0] + \dot{r}_c[1]) / 2.\]  \hspace{1cm} (112)

The process is repeated for the following time steps:

- Determine the velocity of the nanotube at \(t[i]\) by using its position at \(t[i - 1]\) and the fluid velocity as it is at \(t[i]\).
- Approximate the average velocity of the nanotube between \(t[i - 1]\) and \(t[i]\) by the average of the nanotube velocity at \(t[i - 1]\) and \(t[i]\).
- Approximate the nanotube position at \(t[i]\) by changing its position by the product of the average nanotube velocity between \(t[i - 1]\) and \(t[i]\) and the length of time interval \(t[i] - t[i - 1]\).
- Repeat.
References


