Thermophoretic and diffusive gas-phase transport of single-walled carbon nanotubes and their applications in thin film electronics

Patrik Laiho
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Patrik Laiho

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Abstract

Thin films of single-walled carbon nanotubes (SWNTs) show great promise as a building block for transparent conducting films (TCFs), used in display applications, touch sensors and photovoltaic devices, and thin film transistors (TFTs). In contrast to currently used materials, SWNT thin films also maintain their properties under flexing and stretching. Previously, both TFTs and TCFs with performances comparable to currently-used industrial components have been realized using the floating catalyst CVD (FCCVD) method. In the FCCVD method, SWNT growth occurs on catalyst nanoparticles in the gas phase, producing an SWNT aerosol that can be deposited into thin films without dispersion. However, a clearer understanding of the effects of the synthesis conditions on the thin film properties and the transport of SWNT aerosols are still needed to achieve the full potential of the method and the thin films produced using it.

This dissertation focuses in particular on the sampling of SWNTs by thermophoresis, or transport of aerosols by a temperature gradient, and the mechanisms of gas-phase agglomeration, or bundling, of SWNTs during and after FCCVD growth. Thermophoretic deposition avoids previously observed shortcomings related to electrostatic deposition of SWNTs, and facilitates the measurement of unbiased SWNT size distributions, aiding significantly in process development. The bundling of SWNTs in the gas phase and its effects on the TCF performance were studied in unprecedented detail, resulting in a semi-empirical model for TCF performance as a function of the SWNT dimensions and bundle size. Similarly, limiting the catalyst precursor feeding rate was found to decrease bundling in the synthesized SWNTs and result in a clear improvement of the TCF performance. By monitoring the FCCVD process using aerosol measurements, SWNT films with predetermined densities were collected for the fabrication of TFTs with high uniformity, and a stable process concentration was achieved by adjusting catalyst feeding based on the monitoring. As part of this work two thermophoretic precipitators, one used for mechanistic studies and the fabrication of centimetre-scale arrays of TFTs, and a scaled-up unit capable of deposition on ca. 50 mm substrates, were built and tested. Thermophoretic transport of SWNTs was studied experimentally for the first time, and the thermophoretic terminal velocity was found to differ from the free molecular regime model typically used. SWNT TCFs and TFTs fabricated by thermophoretic deposition were shown equivalent or superior performance compared to previously reported devices fabricated by other sampling methods. In addition to thin film applications, the processes and methods developed can be applied in e.g. the basic research of interfaces between SWNTs and other low-dimensional materials and in spectroscopic characterization using methods previously difficult to use with FCCVD SWNTs.

Keywords  single-walled carbon nanotubes; floating catalyst chemical vapor deposition; aerosol technology; aerosol deposition; agglomeration; thermophoresis; transparent conducting films; thin film transistors
Now it reveals its hidden side
and now the other - thus it falls,
an autumn leaf.

Niinpäin, nyt näinpäin,
niinpäin, næinpäin putoaa
vaahteranlehti.

Ryökan Taigu (1758-1831)
translated by Yoel Hoffmann and Kai Nieminen
The work contained in this dissertation has been carried out between the years 2013-2017 in the NanoMaterials Group at the Department of Applied Physics, Aalto University School of Science, led by Professor Esko I. Kauppinen. In a field of research where scientists have a perhaps unfortunate tendency to change their course rapidly at the sight of new, exciting materials, Esko’s choice to focus deeply on a particular set of methods for a long time has been remarkable, but has paid off both in the form of scientific publications and spin-off companies, and hopefully continues to be a source of many interesting discoveries in the future. I wish to particularly thank Esko for providing me with a steady funding, which has given me access to all experimental tools and consumables necessary for carrying out my work, and for access to his extensive network of collaborators, whose comments and support have been highly valuable to me.

The research presented here builds upon the work of many former members of the group, particularly Drs. Albert G. Nasibulin, Antti Kaskela and Kimmo Mustonen. I wish to especially thank Kimmo for all the creative sparring, exchange of research ideas, and comments on writing that have been going on between us during these years. While the peer support and company of all past and present doctoral students of the group have been important to me, I wish to particularly thank Yongping Liao, Aqeel Hussain, and Erxiong Ding for early access to the processes they have been working on and for their help with the final publication of this dissertation. I also wish to thank Dr. Hua Jiang, now the longest standing member of the group outside of Esko, and Drs. Ying Tian and Nan Wei, with whom I shared an office for the past few years, for many interesting conversations and our collaborative research. The help of my research assistants Markus Aapro and Mahdi Rafiee and the administrative support provided by Marita Halme and Reetta Lesonen have also been invaluable to me.

I wish to thank Professor Yutaka Ohno (Nagoya University, Japan) and Professor Shigeo Maruyama (University of Tokyo, Japan), for their coauthorship, encouragement, and the opportunities to visit their research groups during the course of this work. This research has made extensive use of the Aalto University Nanomicroscopy Center and the Aalto NanoFab facilities, and the staff of both must be thanked for keeping their equipment operational and easy to access.

This dissertation is dedicated to my wife Terhen, whose support has been greater and more important to me than that of any other person mentioned, and to my daughter Irene, whose smile and laughter bring light to my days, and whose curiosity and visible enjoyment of learning have been, and continue to be, a great inspiration to me.

Espoo, January 25, 2018
Patrik Laiho
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List of Abbreviations and Symbols

A optical absorbance
AFM atomic force microscopy or microscope
Cc Cunningham slip correction factor
CFD computational fluid dynamics
CPC condensation particle counter
CVD chemical vapor deposition
D diffusion coefficient
db carbon nanotube bundle diameter
dM (diffusive) mobility diameter
dME electrical mobility diameter
dp particle diameter
DMA differential mobility analyzer
e elementary charge
EF Fermi energy
ESP electrostatic precipitator
FCCVD floating catalyst chemical vapor deposition
FCE Faraday cup electrometer
FEM finite element modelling
I_ON/I_OFF ON/OFF current ratio
ITO indium-doped tin oxide
kB Boltzmann’s constant \(1.38064852 \times 10^{-23} \text{ m}^2\text{kg}\text{s}^{-2}\text{K}^{-1}\)
Kφ agglomeration coefficient of a monodisperse aerosol
kγ thermal conductivity of a gas
Kn Knudsen number
LCH thin film transistor channel length (distance between source and drain)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>mean free path (of a gas molecule)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>charge-carrier mobility</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>dynamic viscosity of a gas</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>MNA</td>
<td>modified nodal analysis</td>
</tr>
<tr>
<td>$Q$</td>
<td>volumetric flow rate</td>
</tr>
<tr>
<td>$R_s$</td>
<td>sheet resistance</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>mass density of a gas</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive ion etching</td>
</tr>
<tr>
<td>SDG</td>
<td>spark discharge generator</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy or microscope</td>
</tr>
<tr>
<td>SMPS</td>
<td>scanning mobility particle sizer</td>
</tr>
<tr>
<td>SMPS+C</td>
<td>scanning mobility particle sizer with condensation particle counter</td>
</tr>
<tr>
<td>SMPS+E</td>
<td>scanning mobility particle sizer with electrometer</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-walled (carbon) nanotube</td>
</tr>
<tr>
<td>TCF</td>
<td>transparent conducting film</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy or microscope</td>
</tr>
<tr>
<td>TFT</td>
<td>thin film transistor</td>
</tr>
<tr>
<td>TP</td>
<td>thermophoretic precipitator</td>
</tr>
<tr>
<td>T%</td>
<td>optical transmittance in percents</td>
</tr>
<tr>
<td>$v_{th}$</td>
<td>thermophoretic terminal velocity</td>
</tr>
<tr>
<td>$V_{DS}$</td>
<td>source-drain voltage</td>
</tr>
<tr>
<td>$V_{GS}$</td>
<td>gate voltage</td>
</tr>
<tr>
<td>$W_{CH}$</td>
<td>thin film transistor channel width</td>
</tr>
<tr>
<td>$Z$</td>
<td>electrical mobility of an aerosol particle</td>
</tr>
</tbody>
</table>
This doctoral dissertation consists of an overview and the following publications, which are referred to in the text by their Roman numerals.


III. Kaskela, Antti; Laiho, Patrik; Fukaya, Norihiro; Mustonen, Kimmo; Susi, Toma; Jiang, Hua; Houbenov, Nikolay; Ohno, Yutaka; Kauppinen, Esko I. 2016. Highly individual SWCNTs for high performance thin film electronics. Elsevier. *Carbon*, volume 103, pages 228-234. ISSN 0008-6223. DOI: 10.1016/j.carbon.2016.02.099

IV. Laiho, Patrik; Mustonen, Kimmo; Ohno, Yutaka, Maruyama, Shigeo; Kauppinen, Esko I. 2017. Dry and direct deposition of aerosol-synthesized single-walled carbon nanotubes by thermophoresis. American Chemical Society. *ACS Applied Materials & Interfaces*, volume 9, issue 24, pages 20738-20747. ISSN 1944-8244. DOI: 10.1021/acsami.7b03151

V. Laiho, Patrik; Rafiee, Mahdi; Liao, Yongping; Hussain, Aqeel; Ding, Er-Xiong; Kauppinen, Esko I. Wafer-scale thermophoretic dry deposition of single-walled carbon nanotube thin films. Accepted for publication in the journal *ACS Omega* (12+9 pages).
Author’s Contributions

**Publication I:** Uncovering the ultimate performance of single-walled carbon nanotube films as transparent conductors

The author co-designed the experimental concept with the first author of the publication, carried out the scanning electron and atomic force microscopy and analysis of the micrographs, and contributed to the interpretation of the results and the writing of the manuscript.

**Publication II:** Toward the limits of uniformity of mixed metallicity SWCNT TFT arrays with spark-synthesized and surface density controlled nanotube networks

The author carried out the scanning electron and atomic force microscopy and analysis of the micrographs, wrote the code for analyzing the thin film transistor measurements, wrote and carried out the numerical simulations, and contributed to the interpretation of the results and the writing of the manuscript.

**Publication III:** Highly individual SWCNTs for high performance thin film electronics

The author co-designed the experimental concept with the first author of the publication, carried out the electron and atomic force microscopy and analysis of the micrographs, wrote the code for analyzing the thin film transistor measurements and contributed to the interpretation of the results and the writing of the manuscript.

**Publication IV:** Dry and direct deposition of aerosol-synthesized single-walled carbon nanotubes by thermophoresis

The author carried out all experiments, designed and built the deposition system, analyzed and interpreted the data and wrote the manuscript. The co-authors commented on the interpretation of the results and the manuscript.

**Publication V:** Wafer-scale thermophoretic dry deposition of single-walled carbon nanotube thin films

The author designed the experimental concept and the deposition system used in the experiments, which was partially based on an existing electrostatic precipitator. The construction of the deposition system and the sample deposition were carried out jointly with the second author of the publication, whose work the author supervised. The author characterized the thermophoretically deposited samples, carried out the finite element modelling, analyzed and interpreted the data and wrote the manuscript. The other authors contributed to the materials synthesis, the collection and characterization of the samples collected by filtering, and the testing of the deposition system, and commented on the experimental design and the manuscript.
Other featured publications

The author has also contributed to the following publications:

- Susi, Toma; Kaskela, Antti; Zhu, Zhen; Ayala, Paola; Arenal, Raul; Tian, Ying; Laiho, Patrik; Mali, Juha; Nasibulin, Albert G.; Jiang, Hua; Lanzani, Giorgio; Stephan, Odile; Laasonen, Kari; Pichler, Thomas; Loiseau, Annick; Kauppinen, Esko I. 2011. Nitrogen-doped single-walled carbon nanotube thin films exhibiting anomalous sheet resistances. American Chemical Society. Chemistry of Materials, volume 23, issue 8, pages 2201-2208. ISSN 0897-4756. DOI: 10.1021/cm200111b.


- Mustonen, Kimmo; Laiho, Patrik; Kaskela, Antti; Zhu, Zhen; Reynaud, Olivier; Houbenov, Nikolay; Tian, Ying; Susi, Toma; Jiang, Hua; Nasibulin, Albert G.; Kauppinen, Esko I. 2015. Gas phase synthesis of non-bundled, small diameter single-walled carbon nanotubes with near-armchair chiralities. AIP Publishing. Applied Physics Letters, volume 107, issue 1, article number 013106 (5 pages). ISSN 0003-6951. DOI: 10.1063/1.4926415

- Ding, Er-Xiong; Jiang, Hua; Zhang, Qiang; Tian, Ying; Laiho, Patrik; Hussain, Aqee; Liao, Yongping; Wei, Nan; Kauppinen, Esko I. 2017. Highly conductive and transparent single-walled carbon nanotube thin film from ethanol by floating catalyst chemical vapor deposition. Royal Society of Chemistry. Nanoscale, volume 9, issue 44, pages 17601-17609. DOI: 10.1039/C7NR05554D
• Qiang, Zhang; Wei, Nan; Laiho, Patrik, Kauppinen, Esko I. Recent developments in thin single-walled carbon nanotube films fabricated by dry floating catalyst chemical vapor deposition. Springer International Publishing. *Topics in Current Chemistry*, volume 375, issue 6, article number 90. DOI: 10.1007/s4106

• Held, Martin; Laiho, Patrik; Kaskela, Antti; Gannott, F.; Rother, Marcel; Kauppinen, Esko I.; Zaumseil, Jana. 2017. Dense Carbon Nanotube Films as Transparent Electrodes in Low-Voltage Polymer and All-Carbon Transistors. Accepted for publication in the journal *Advanced Electronic Materials*. DOI: 10.1002/aelm.201700331

• Tian, Ying; Jiang, Hua; Laiho, Patrik; Kauppinen, Esko I. On the Validity of Measuring Metallic and Semiconducting SWCNT Fractions by Quantitative Raman Spectroscopy. Accepted for publication in the journal *Analytical Chemistry*. DOI: 10.1021/acs.analchem.7b03712

• Ahmad, Saeed; Laiho, Patrik; Zhang, Qiang; Jiang, Hua; Hussain, Aqeel; Liao, Yongping; Ding, Er-Xiong; Wei, Nan; Kauppinen, Esko I. Time stable gas phase synthesis of metallic and bimetallic catalyst nanoparticles by rod to tube type spark discharge generator. Submitted to the journal *Journal of Aerosol Science* in the year 2017.

• Hussain, Aqeel; Liao, Yongping; Zhang, Qiang; Ding, Er-Xiong; Laiho, Patrik; Ahmad, Saeed; Wei, Nan; Tian, Ying; Jiang, Hua; Kauppinen, Esko I. Floating Catalyst CVD Synthesis of Single Walled Carbon Nanotubes from Ethylene for High Performance Transparent Electrodes. Submitted to the journal *Nanoscale* in the year 2018.
1. Introduction

The National Nanotechnology Initiative of the United States defines nanotechnology as the imaging, measuring, modeling, and manipulation of matter at the length scale of approximately 1 and 100 nanometers (10^{-7} to 10^{-9} meters). In this size range, or the nanoscale, the physical properties of structures, such as their electrical and thermal conductivity, are qualitatively different from the bulk properties of the materials they consist of and new emergent properties not present in the bulk material, with novel technological applications, may arise. The properties of nanoscale structures have been utilized by humanity without a complete understanding of the underlying mechanisms since antiquity, and nanoscale functional structures are ubiquitous in biology. However, by the end of the last century, techniques of materials growth, characterization and simulation had advanced to the point, where such structures could be reliably fabricated and identified and their properties could be predicted. This in turn led to the adoption of neologisms such as nanotechnology and nanoscience, and the ongoing enormous research efforts on nanoscale materials and devices.

![Figure 1.1](image_url)

*Figure 1.1. a) Proportion of surface atoms in face-centered cubic (FCC) nanoparticles. The depicted particles are a 13-atom particle with a diameter of ca. 0.74 nm, a 309-atom particle with a diameter of ca. 2.2 nm and a larger cuboctahedral particle. Adapted from Poole and Owens\(^1\). b) The melting point of gold nanoparticles as a function of their diameter. Adapted from Johnston\(^2\).*

As an illustrative example of qualitative changes in the nanoscale, when a metal is in the form of nanoparticles, or particles with a diameter of a few nanometers, it has a much higher catalytic activity and lower melting point compared to its bulk properties. This results simply from the fact that in nanoparticles, a significantly higher number of metal atoms are located on the surface, and as a result can catalyze a chemical reaction. Likewise, surface atoms have smaller bonding energies to the lattice, so a larger proportion of surface atoms leads to a lower melting point. An estimate of the proportion of surface atoms in face-centered cubic nanoparticles
(which could be e.g. crystalline gold or iron nanoparticles), and an empirically based dependency between the diameter and melting point of gold nanoparticles are presented in Figure 1.1.

As a practical example of the use of nanoparticles as catalysts, iron nanoparticles are used as a catalyst for the growth of single-walled carbon nanotubes by the disproportionation of carbon monoxide in the work contained in this dissertation.

An important qualitative change in nanometer-scale structures is that the quantum mechanical nature of electrons becomes significant. When one or more dimensions of a metal or semiconductor structure is shrunk to the scale of the electron de Broglie wavelength, the wave function describing the behavior of electrons in the structure behaves as if confined to a potential well along those dimensions. This effect, called quantum confinement, causes the electronic structures of nanostructures to differ dramatically from their three-dimensional counterpart, and quasi-two-, one- and zero-dimensional structures, where one, two or three spatial dimensions are confined this way, are sometimes called quantum wells, quantum wires and quantum dots, respectively. Likewise, in low-dimensional structures such as segments of carbon nanotubes, where the mean free path, or distance between scattering events, of moving electrons is large compared to the dimensions of the structure, electrical conductance becomes quantized and independent of the length of the structure. The sharp peaks in the electron density of states of 1D quantum wires and the discrete energy spectrum of 0D quantum dots result in sharp optical absorption and emission peaks, which have, particularly in the case of quantum dots, a multitude of optical applications, since the band can be tuned by changing the physical size of the quantum dot. This property of nanoparticles has been utilized since antiquity by glassmakers, whose (empirically discovered) recipes for colored glasses practically amount to the addition of colloidal metal nanoparticles in the glass. In the present day, quantum dots in the form of semiconductor nanoparticles of different sizes are used in thin film displays as emitters of pure, or narrow-band red, green and blue light.

![Figure 1.2. Sketches of the density of states in three-dimensional and (quasi-) two-, one- and zero-dimensional structures. The sharp peaks in the density of states of quasi-one-dimensional structures such as single-walled carbon nanotubes are called van Hove singularities.](image)

Starting in the 1980s, several new allotropes of carbon with low-dimensional molecular structures were discovered and their properties described. These include the near-spherical or polyhedral fullerenes, single- and multi-walled carbon nanotubes (CNTs, SWNTs, MWNTs) and
isolated layers of graphene. In these, sp² bonded carbon forms a polyhedral cage, single or multiple closed cylindrical surfaces, or a flat, atomically thin sheet, respectively. The current interest in CNTs sparked after their structure was reliably identified³–⁴ and their properties theoretically studied⁵–⁷ in the 1990s, although the earliest reports about the material date back to 1952⁸. Carbon nanotubes and graphene have attracted widespread attention due to their intrinsically low-dimensional structure, which makes it possible to use them as a molecular building block for nanoscale electronic and photonic devices, and due to their high electrical and thermal conductivity and mechanical strength. The electrical, thermal and mechanical properties make them also interesting as additives or reinforcers in composite materials.

![Figure 1.3. Low-dimensional allotropes of carbon. a) A C₆₀ buckminsterfullerene. b) A single-walled carbon nanotube. c) A single sheet of graphene. Rendered using VMD⁹ (http://www.ks.uiuc.edu/Research/vmd/), a molecular visualization program developed at the University of Illinois Urbana-Champaign and distributed free of charge.](image)

The electronic properties of SWNTs are highly sensitive to their specific molecular structure, described in Chapter 2.1, and their applicability in e.g. micro- and nanoelectronics is hindered by the fact that SWNTs with a single specific structure cannot be reliably produced at the moment of writing. However, this is not an issue in applications such as composite materials reinforced by MWNTs or SWNTs, and electronics based on SWNT thin films, where complete control over the structure of the nanotubes is typically not needed. At the moment of writing, SWNTs are reaching commercial end use in both applications. Thin films of SWNTs show particular promise as transparent conducting films (TCFs) utilized widely in liquid crystal displays, touch-sensing elements, photovoltaic devices and organic light-emitting diodes, since their electrical and optical properties are close to the transparent and conductive doped metal oxides currently used in the industry¹⁰. Unlike these materials, thin films of SWNTs are mechanically robust and preserve their properties well under stretching or bending, making it possible to use them in thin film electronics fabricated on flexible and stretchable substrates. SWNT thin films have also attracted wide attention as a semiconductor material for thin film transistors (TFTs), since their electrical properties exceed those of organic semiconductors and amorphous silicon, are on par with low-temperature polycrystalline silicon, and are in principle suitable for applications such as display switching and radio-frequency wireless communications¹¹.
On a general level, aerosol-based, or gas-phase, synthesis methods are an attractive way of producing nanoparticles and other nanomaterials, and are used commercially in the manufacturing of e.g. carbon black, pigments, and battery electrodes. As particular advantages, aerosol-based methods typically do not produce liquid byproducts and allow for real-time process monitoring of the using aerosol measurement tools and relatively easy collection of the end product using filtration or aerosol deposition. Additionally, in some size ranges, the product can be fractionated based on its size. In this dissertation, a floating catalyst chemical vapor deposition (FCCVD) process, where a carbon feedstock is catalytically decomposed on the surface of aerosol catalyst nanoparticles, is used to synthesize single-walled carbon nanotubes for the fabrication of thin films and for the study of their aerosol dynamics and deposition. The central topics of research have been bundling, or the agglomeration of SWNTs during after synthesis, the diffusive and thermophoretic transport of SWNT aerosols and a direct, dispersion-free fabrication process for SWNT thin films based on deposition by thermophoretic precipitators. More specifically, the following research questions have been studied:

• What is the mechanism causing agglomeration, or bundling of SWNTs in the gas phase and the effective size determining their rate of agglomeration?
• What is the effect of the SWNT bundle size on the performance of transparent conducting films made of SWNTs?
• Can aerosol measurement tools be used to monitor the state of a FC-CVD synthesis process and deposit SWNT thin films with predetermined surface densities?
• What is the thermophoretic transport mechanism and resulting thermophoretic velocity of SWNT aerosols?
• What are the properties of SWNT thin films fabricated by thermophoretic deposition of aerosol-synthesized SWNTs compared to thin films deposited using other methods?

In Publication I, the first question is studied using a modification of the floating catalyst CVD process, where the SWNT aerosol is deliberately agglomerated by passing it through an agglomeration chamber, or a transport line with a long residence time. The agglomeration of the SWNT aerosol is found to correspond well to the textbook model of diffusive agglomeration of monodisperse aerosols, when an effective mobility diameter between 10-20 nm is used for the SWNT aerosol in question. The second question is studied also in Publication I and Publication III, and a semiempirical model relating the transparent conducting film performance and the mean bundle size and SWNT length has been developed based on the findings of Publication I. In general, an increase in the bundle size is shown to have an adverse effect on the thin film performance. In Publications II and IV, the number concentration of the aerosol produced by the process is measured using condensation particle counters and scanning mobility particle sizers, and the deposition of SWNT thin films with predetermined surface densities based on aerosol measurements is demonstrated. Finally, in Publications IV and V, SWNT TFTs and TCFs are fabricated using thermophoretic deposition, and the method is shown to produce SWNT thin films with properties that are comparable to previously published films deposited using filtering. Based on Publication V, the thermophoretic deposition method is scalable to a wafer-scale or roll-to-roll process in a straightforward manner and shows particular promise in the deposition of SWNT TCFs on polymer substrates.
This dissertation is organized into five chapters. **Chapter 1**, the research is motivated and put into context, and the main findings are summarized. **Chapter 2** describes the basic structural, electrical and optical properties of SWNTs and the properties of SWNT thin films relevant to this dissertation, and reviews select parts of earlier research on SWNT thin films. **Chapter 3** describes the aerosol physics relevant for interpreting the obtained results, mainly Brownian diffusive transport and agglomeration, thermophoretic transport, and electrostatic transport. More complete descriptions of aerosol dynamics, transport, and measurement techniques are available *e.g.* in the textbooks by Hinds13 and Friedlander14. **Chapter 4** describes the experimental techniques and tools utilized in this work and their mechanistic basis, when it has not been covered in **Chapters 2** and **3**. Finally, **Chapter 5** recaps the main results of the publications contained in this dissertation and discusses possible directions for future research based on them.
2. Single-walled carbon nanotubes

2.1 Structural and electronic properties

Carbon has the electron configuration $1s^22s^22p^2$. In covalently bonded two-dimensional layers of carbon, such as a graphene sheet and the surface of a SWNT, the $2s$ orbital and the $2p_x$ and $2p_y$ orbitals form three hybridized $sp^2$ orbitals in the plane at $120^\circ$ angles relative to each other, resulting in a characteristically hexagonal graphene lattice, where each atom has three neighbors. These orbitals form strong $\sigma$ bonds and the remaining $2p_z$ orbital is perpendicular to the surface, forming metallic $\pi$ bonds with the $2p_z$ orbitals of neighboring carbon atoms. The $\pi$ electron system, with highly mobile delocalized electrons, results in a very high charge carrier mobility and electrical and thermal conductivity. Mechanically, the high $\sigma$ bond strength results in a very high in-plane Young’s modulus on the order of 1 TPa\textsuperscript{15}, making CNTs one of the stiffest known materials, and a tensile strength of ca. 150 GPa\textsuperscript{16}.

A single-walled carbon nanotube (SWNT) can be thought of as a strip of the hexagonal graphene lattice, which has been folded into a closed cylindrical surface. Despite the popularity of this figure of speech, no known method of SWNT synthesis actually proceeds this way. Meanwhile, thin strips of graphene, or nanoribbons, have been produced by “unzipping” SWNTs\textsuperscript{17}. The width of the strip and the angle at which it has been “cut” from the lattice can be described by a chirality vector $C = na_1 + ma_2$, where $a_1$ and $a_2$ are the unit vectors of the graphene lattice. Graphical depictions of the unit vectors and the coefficients $n$ and $m$ are shown in Figure 2.1.1. For example, in a SWNT with $(n,m) = (5,2)$, the axis orthogonal to the tube axis corresponds to a vector $5a_1 + 2a_2$. SWNTs with $n = m$ are referred to as “armchair” nanotubes due to the pattern traced by the chirality vector, and correspondingly, SWNTs with $n = 0$ are referred to

![Figure 2.1.1.](image)
as “zigzag” nanotubes. In other cases, the nanotubes are said to be chiral, and the hexagonal pattern spirals along the tube’s cylindrical axis at an angle

$$\theta = \tan^{-1} \left( \frac{m\sqrt{3}}{m+2n} \right)$$ \hspace{1cm} (2.1.1)$$

relative to the unit vector \(a_\mu\). The diameter of a SWNT is given by

$$d = \frac{a}{\pi} \sqrt{n^2 + nm + m^2},$$ \hspace{1cm} (2.1.2)$$

where \(a = 0.246 \text{ nm}\) is the length of the unit vectors \(a_1\) and \(a_2\). An additional detail, not covered by the chirality vector, is that the SWNT structure may be either open or capped by a half-spherical fullerene structure. The form factors of carbon nanotubes can be very large, since their diameter is on the order of magnitude of one nanometer, while their length may be up to hundreds of micrometers or even more. The chirality of a given nanotube may be determined directly using scanning tunneling microscopy (STM) or high-resolution transmission electron microscopy (TEM), both of which can in principle resolve the atomic structure of the SWNT surface. However, the difficulty of preparing a suitable sample, the slow throughput of both methods and the issue of beam damage in TEM make this impractical and in practice, electron diffraction patterns obtained using TEM\(^3\)-\(^19\), or a variety of optical spectroscopic methods, the most common of which are covered in Chapter 2.2., are used to characterize the contents of SWNT samples.

The electronic properties of SWNTs can be thought of as a further quantization of the two-dimensional electronic properties of a graphene sheet. The electronic states of graphene are two-dimensional, with nearly continuously varying momenta in the \((k_x, k_y)\) plane, but with only a single allowed value for \(k_z\). The electronic band structure of graphene was first derived by Wallace\(^20\) using a tight-binding model, resulting in the dispersion relation

$$E_{\pm}(\vec{k}) = \pm t \sqrt{3 + f(\vec{k}) - t' f(\vec{k})},$$ \hspace{1cm} (2.1.2)$$

where the positive sign applies to the upper \(\pi^*\), or conduction, band and the negative sign to the lower \(\pi\), or valence, band, \(t\) and \(t'\) are tight binding parameters and

$$f(\vec{k}) = 2 \cos(\sqrt{3}k_\gamma a) + 4 \cos\left(\frac{\sqrt{3}}{2} k_\gamma a\right) \cos\left(\frac{3}{2} k_\lambda a\right),$$ \hspace{1cm} (2.1.3)$$

where \(a\) is the hexagonal lattice constant. A visualization of Eqs. 2.1.2 is shown in Figure 2.1.2.

Near the high symmetry corners \(k = \vec{K}\) of the first Brillouin zone, commonly called the Dirac points, the dispersion relation can be approximated using \(\vec{k} \approx \vec{K} + \vec{k}'\) as

$$E_{\pm}(\vec{k}') \approx \pm \hbar v_F |\vec{k}'|,$$ \hspace{1cm} (2.1.4)$$

where \(\vec{k}'\) is the momentum vector relative to \(\vec{K}\) and \(\frac{3ta}{2\hbar} = v_F \approx 8 \times 10^5 \text{ m/s}\) is the Fermi velocity. Importantly, these unusual features lie in the immediate vicinity of the Fermi energy \(E_F\). Whereas bulk metals typically have spherical Fermi surfaces with a large set of available quantum states, graphene has a Fermi “surface” composed of a discrete set of exactly six allowed
momenta. As a result, graphene is sometimes referred to as a “semimetal”, or a zero-band gap semiconductor.

The graphene sheet may be further reduced to an electronically one-dimensional material by cutting a narrow strip, commonly called a graphene nanoribbon out of it, and possibly “rolling” the strip into a closed tube, thus forming in principle an SWNT, as discussed earlier. If the width of the strip is \( j \) carbon atoms, then \( j \) sub-bands, each corresponding to a wave vector parallel with the tube’s major axis, constitute the set of allowed states. In the case of a nanoribbon, the electronic structure and electron transport along the strip are complicated by the strip’s boundaries, which effectively act as a hard-wall potential, not present in the closed geometry of an SWNT\(^{21}\).

Figure 2.1.2. The one-dimensional quantization of the graphene band structure, given by Eq. 2.1.2., in the case of a metallic (top row) and a semiconducting (bottom row) SWNT. a) and b) depict the cross-sections of the graphene band structure in the case of an armchair nanotube, in which some of the sub-bands, depicted by the dashed lines, intersect the \( \mathbf{K} \) symmetry points, resulting in a metallic band structure (c). The bottom row depicts the cross-sections in the case of a chiral nanotube, in which the dashed lines depicting the sub-bands miss all of the \( \mathbf{K} \) points, and the band structure (f) is semiconducting. Based on Wallace\(^{20}\) and Dresselhaus and Avouris\(^{22}\).

Depending on its chirality, a single-walled nanotube can be either metallic or semiconducting. In armchair SWNTs, with \( m = n \), the \( j = 0 \) sub-band, situated at \( k_x = 0 \) in the case of the armchair SWNT, and additional sub-bands intersect the \( \mathbf{K} \) point, making such SWNTs metallic conductors. In SWNTs with \( m \neq n \), the \( j = 0 \) sub-band will not cross a \( \mathbf{K} \) point, but one of the other sub-bands may do so. It follows from geometry that when \( (m-n) \mod 3 = 0 \), one of the sub-bands intersects a \( \mathbf{K} \) point and causes the SWNT to be metallic. Correspondingly, in SWNTs where \( (m-n) \mod 3 \neq 0 \), the allowed sub-bands will not intersect any \( \mathbf{K} \) points, making such tubes semiconducting. Because, according to Eq. 2.1.3. the energy dispersion relation of graphene is linear with regards to \( k \) near the \( \mathbf{K} \) point, the energy gap of the states not intersecting a \( \mathbf{K} \) point is proportional to the subband spacing \( \Delta k \). Since \( \Delta k \) is determined by the diameter
of the SWNT (or analogously, the width of a graphene nanoribbon) and the fixed lattice constant $a$, the band gap of a semiconducting SWNT is determined solely by its diameter $d$, and follows approximately the rule of thumb

$$E_g = (0.85 \text{ eV})/d,$$  \hspace{1cm} (2.1.5)

where $d$ is the diameter of the SWNT in nanometers. Additionally, curvature-induced strain may induce small gaps in the electronic structure of metallic SWNTs with $n \neq m$, but the induced gaps have energies well below the thermal energy $k_B T$ at room temperature. In the case of SWNTs with diameters higher than 1.0 nm, these effects can generally be ignored.

The density of states of SWNTs follows directly from their characteristic electronic band structure. The $i$th sub-band of a SWNT has the dispersion relation

$$E_i(k) = \pm \sqrt{(\hbar v_F k)^2 + \left(\frac{\epsilon_{gi}^i}{2}\right)^2},$$  \hspace{1cm} (2.1.6)

where $\epsilon_{gi}^i$ are the individual band gaps of each sub-band, determined by the distance to the nearest $K$ point. The corresponding density of states

$$g(E) = \sum g_i(E), \quad g_i(E) = \frac{4}{\pi \hbar v_F} \left[1 - \left(\frac{\epsilon_{gi}^i}{2E}\right)^2\right]^{\frac{1}{2}},$$  \hspace{1cm} (2.1.7)

shows distinctive van Hove singularities characteristic of a one-dimensional electronic structure. The factor of 4 in $g_i(E)$ accounts for the fourfold (spin and orbital) degeneracy of each sub-band.

### 2.2 Optical properties

Due to the one-dimensional density of states described in Chapter 2.1, the optical absorption spectra of SWNTs contain strong and narrow absorption peaks caused by electronic transitions in the SWNTs. These are widely used to characterize the electronic types and diameters of SWNTs in a sample, and optical absorption spectroscopy has been used to determine the mean diameter of SWNT samples in all publications included in this dissertation.

Optical transitions occurring between the $v_1 - c_1, v_2 - c_2, etc.$ van Hove singularities of semiconducting and metallic nanotubes are normally labeled as $S_{11}, S_{22}, M_{11}, etc.$, or if the electronic type of the tube is unknown or unimportant, as $E_{11}, E_{22}, etc.$ The crossover transitions $c_1 - v_2, c_2 - v_1, etc.$, are comparably very weak, because they are forbidden by optical selection rules and thus do not contribute significantly to the absorption spectrum under normal circumstances.
The transition energies of different SWNTs can be presented in a so-called Kataura plot\textsuperscript{25}, which can in principle be used to assign a specific absorption peak to a specific chirality, or to determine the approximate mean diameter of a sample of SWNTs based on the locations of their optical absorption peaks. A Kataura map, limited to the S\textsubscript{11}, S\textsubscript{22}, and M\textsubscript{11} transitions for clarity and based on tight-binding calculations of the density of states, and a representative optical absorption spectrum of a SWNT thin film sample are presented in Figure 2.2.2. In addition to the electronic transition peaks, the optical absorption spectrum typically also contains a strong $\pi$ plasmon absorption peak, associated with the collective oscillation of the $\pi$ electrons in carbon, in the ultraviolet region at ca. 5 eV, which also contributes to the background at the SWNT optical transition energies. In practice, the transition energies may be shifted \textit{e.g.} by curvature and many-body effects, and interactions with the environment, and modified tight-binding models\textsuperscript{26} and charts of empirically determined optical transitions\textsuperscript{27-28} have been published.

In addition to their characteristic optical absorption features, resonant Raman spectroscopy is often used to characterize SWNT samples due to several signatures that are specific to SWNTs and, together with optical absorption spectroscopy, has been used to determine the mean diameters of SWNTs in \textit{Publication III}. Resonant Raman spectroscopy is based on the
inelastic Raman scattering of photons from optical phonons corresponding to vibrational states in a molecule. Normally, the probabilities of inelastic scattering events are extremely low, since the corresponding electronic transition happens to a virtual state with a short lifetime. However, when the incident photon energy ($h \nu$) or scattered photon energy ($h \nu \pm h \omega$) matches the energy separation of two electronic states, it is said to be in resonance and the probability of the scattering process is increased by a factor of approximately $10^3$ compared to a non-resonant process.

A detailed description of the Raman scattering processes and signatures present in SWNTs is given in Dresselhaus et al. Typically, SWNT samples are characterized using two different first-order (involving one scattering event and phonon) Raman processes called the RBM mode (for “radial breathing mode”) and G mode (for “graphite”). The RBM mode is specific to SWNTs and corresponds to a coherent “breathing” vibration, in which the carbon atoms move together in the radial direction of the tube. Since the mass of carbon atoms along the circumferential direction of the SWNT is proportional to the diameter, a rule of thumb

$$\omega_{RBM} = \frac{248 \text{ cm}^{-1}}{d}, \quad (2.2.1)$$

where $\omega_{RBM}$ is the Raman shift in wavenumbers and $d$ is the SWNT diameter in nanometers, can be used for the RBM wavenumber of isolated SWNTs on a SiO$_2$ substrate. More accurate values, accounting for SWNT-SWNT and SWNT-substrate interactions, have also been reported.

Figure 2.2.3. a) Kataura plot for resonant Raman spectroscopy. The blue circles indicate semiconducting SWNTs and orange squares metallic SWNTs. Three typically excitation wavelengths are shown as horizontal lines. The upper $x$ axis indicates RBM wavenumbers assigned using Eq. 2.2.1 and the lower $x$ axis the SWNT diameter. Based on tabulated data by S. Maruyama, calculated based on Saito et al. Used with permission. b) A representative Raman spectrum from a SWNT thin film, obtained at an excitation wavelength of 514 nm. Data courtesy of Aqeel Hussain.

The G band corresponds to in-plane vibrations in the graphene lattice and in the case of graphene, is observed at $\omega = 1582$ cm$^{-1}$. In SWNTs, the G band is split into two sub-bands due to curvature, one corresponding to lattice vibrations in the direction of the SWNT axis, called the G’ mode, and the other to vibrations in the circumferential direction, called the G’’ mode.

In addition to the two first-order processes described above, the D (for “disorder”) band at $\omega = 1350$ cm$^{-1}$ corresponding to a second-order (arising from the scattering of excited phonons) Raman scattering process, is commonly used in the Raman spectroscopic characterization of
SWNT samples. The D band is associated with defects and discontinuities in the graphene lattice of the SWNT walls, and thus the intensity ratio of the G and D band Raman signatures is commonly used to determine the quality of a SWNT sample. Due to the strong dependency on the resonance condition (typically, a resonance window of 100 meV is assumed\textsuperscript{29}), the number and type of SWNTs that can be detected by Raman spectroscopy are limited by the excitation energy, and in practice multiple excitation wavelengths are used. However, even with multiple excitation energies, quantifying the types of SWNTs present in a sample reliably using Raman spectroscopy is difficult due to the tightness of the resonance condition. A Kataura plot for resonant Raman spectroscopy, based on tight-binding calculations of the electronic transitions, and a representative Raman spectrum measured from an SWNT thin film sample similar to those studied in this dissertation, are given in Figure 2.2.3.

Semiconducting SWNTs show also characteristic photoluminescence behavior, widely used to characterize the contents of samples and also in emerging photonic applications. Since this property is not used in the research contained in this dissertation, it is covered just briefly. When the SWNT absorbs a photon through the $S_{22}$ transition, a strongly bound exciton, or hole-electron pair, is formed at the states $c_2, v_2$, and relaxed through a phonon-mediated process to $c_1, v_1$. The recombination of the exciton then results in the emission of a photon with an energy corresponding to the $S_{11}$ transition. The formation of strongly bound excitons in SWNTs is an additional consequence of their quasi-one-dimensional electronic properties, specifically the confinement of Coulomb interaction to one dimension. In practice, photoluminescence is easily quenched by interactions between the SWNTs and their surroundings and can be detected only from semiconducting SWNTs that are well insulated from substrates and adjacent SWNTs, e.g. when suspended on a trench structure\textsuperscript{30}, or within surfactant micelles\textsuperscript{31}. By scanning the excitation and emission wavelength, a photoluminescence map similar to that depicted in Figure 2.2.4b can be obtained.

**Figure 2.2.4.** a) A schematic of the photoluminescence mechanism of semiconducting SWNTs. The absorption of a photon leads to the formation of an exciton at the $c_2, v_2$ state, which then relaxes to the $c_1, v_1$ state through a phonon-assisted process and recombines to emit a photon. b) A representative PL map measured from an individual air-suspended SWNT similar to those studied in Publications I and II. Unpublished data, courtesy of Akihiro Ishii and Yuichiro Kato, RIKEN. The measurement setup is described in detail in Ishii et al.\textsuperscript{32}

### 2.3 Synthesis and processing

In the seminal works describing their structure, SWNTs were synthesized using so-called physical methods, in which a carbon-containing target, typically graphite, is evaporated to release free atomic carbon, which then self-assembles into a graphitic network. Sufficient energy for
the evaporation can be provided by an electric arc discharge or a pulsed laser beam. Both methods produce a mixture of different carbon allotropes including amorphous carbon, and SWNTs can be produced if the carbon target if alloyed with a catalyst material, typically a transition metal.

SWNTs can be grown selectively using a number of catalytic chemical vapor deposition (CVD) processes. In these, a carbon-containing precursor, or feedstock, is catalytically decomposed on the surface of catalyst particles, and the specific process conditions and catalyst morphology determine whether SWNTs or MWNTs are grown. In supported or substrate CVD processes, the catalyst is deposited on a temperature-resistant support in the form of particles or stripes, and the support is placed inside a high-temperature (typically 600-1200°C) furnace. Typically, small-molecule hydrocarbons such as methane (CH₄), acetylene (C₂H₂), ethylene (C₂H₄), or ethanol (C₂H₅OH), or carbon monoxide (CO) are used as the feedstock and transition metals (iron, nickel, cobalt, molybdenum and their alloys) are used as the catalyst, for decomposition reactions of the general form

\[ C_xH_y \rightleftharpoons xC + \frac{y}{2}H_2, \quad (2.3.1) \]

or, in the case of CO, the reactions

\[ CO + CO \rightleftharpoons C + CO_2; \quad CO + H_2 \rightleftharpoons C + H_2O. \quad (2.3.2) \]

Sulfur, typically in the form of thiophene, or weak oxidizers such as water are commonly used as growth promoters. The catalyst is commonly pretreated in a reducing hydrogen atmosphere, and hydrogen can be included in the process atmosphere to prevent the thermal self-decomposition of the carbon feedstock, which leads to unwanted side products. While the slow kinetics of the CO disproportionation reaction limit the growth rate achievable using CO as the carbon feedstock, it has the advantage that, unlike hydrocarbons, CO has no thermal self-decomposition reaction which would otherwise lead to the formation of unwanted amorphous carbon. CVD processes may operate either at an elevated pressure, at atmospheric pressure or in partial vacuum, and plasma enhancement can be used to further increase the reactivity of the precursors. In highly reactive conditions, the growing SWNTs form vertically aligned structures, and otherwise they are typically confined to the substrate surface. The direction and placement of SWNTs grown using substrate CVD processes cannot be normally controlled to a high extent, but on certain substrates such as a-plane sapphire or ST cut quartz, highly aligned SWNTs following the crystalline direction of the substrate, useful for optical and electronic applications, can be grown.

In floating catalyst CVD (FCCVD) processes, the catalyst material is in the form of a nanoparticle aerosol, on which the CVD reactions happen without a support. The catalyst particles may be produced from the dissociation of a metal-containing precursor (typically an organo-metallic compound such as ferrocene or iron pentacarbonyl), which may be fed to the reactor as a sublimated vapor or mixed in a liquid carbon feedstock, or by means of a physical catalyst source such as a hot filament or a spark discharge. The carbon feedstocks are similar to substrate CVD processes, and the reactors may either operate at atmospheric pressure or at elevated pressures, to increase the reactivity of the precursors (e.g. to compensate for the slow kinetics of the CO disproportionation reaction). The reactor product may be collected by
scraping it from the internal walls of the reactor\textsuperscript{37}, by filtering the reactor effluent\textsuperscript{46}, by collecting it using other aerosol sampling tools such as the thermophoretic precipitators described in \textbf{Publications IV} and \textbf{V}, or if the process is operated at a high enough SWNT number concentration to form an aerogel-like structure, it can be extracted from the reactor continuously\textsuperscript{47}.

In the publications contained in this dissertation, atmospheric pressure FCCVD processes, with CO as the carbon feedstock, were used for SWNT growth. In \textbf{Publications I} and \textbf{II}, the catalyst nanoparticles were produced using a spark discharge generator (SDG), and in \textbf{Publications III–V}, using ferrocene as the catalyst precursor. Detailed descriptions of the synthesis processes and conditions used are presented in Chapter 4.1. The nucleation, growth, and growth termination mechanisms of SWNTs in the FCCVD process are mainly not within the scope of this work, but have been extensively discussed in the literature. Jourdain and Bichara\textsuperscript{48} have published a relatively recent review on the general mechanisms of catalytic CVD growth of SWNT, and early mechanistic studies and reviews concerning growth processes similar to those used in this have been published by Moisala \textit{et al.}\textsuperscript{39}, Nasibulin \textit{et al.}\textsuperscript{49} and Anisimov \textit{et al.}\textsuperscript{50}. It should be noted that certain key questions, such as the microscopic mechanisms of SWNT nucleation from the catalyst particle, and the observation of preferred growth of certain, usually near-armchair, chiralities in many processes, are still under active study at the moment of writing.

\textbf{Figure 2.3.1.} Schematic of the catalyst formation and SWNT nucleation and growth in the floating catalyst CVD process using CO as the carbon feedstock. Partially based on Moisala \textit{et al.}\textsuperscript{39} and Moisala \textit{et al.}\textsuperscript{51}
A sketch of a FCCVD growth process similar to those used in this work is presented in Figure 2.3.2. First, a vapor of elemental iron, either produced by the physical evaporation of iron in the spark discharge generator or the thermal decomposition of ferrocene in the top part of the reactor, nucleates into catalyst nanoparticles. At higher-temperature parts of the reactor, the CO disproportionation reaction introduces elementary carbon into the particles, where it dissolves until the particle is saturated. At supersaturation, carbon starts to precipitate on the particle surface and forms sp² bonded chains, until a carbon cap is formed on the surface of the particle. Under favorable conditions, the carbon cap detaches from the catalyst particle and more carbon, in the form of sp² carbon chains, is incorporated in the growing SWNT by covalent bonding. Under stable conditions, the growth is expected to continue as long as the residence time in the suitable temperature zone of the FCCVD process permits, although bundling due to SWNT-SWNT collisions likely disturbs the steady-state growth conditions and may lead to slowing or termination of the growth. In Publication III, this mechanism is suggested to be behind the observed SWNT length distributions.

Bulk samples produced by high-yield implementations of the processes discussed, and commercially available SWNTs, are typically in the form of powders or liquid dispersions made from them. A particular hindrance for the applications of SWNTs has been that they are practically insoluble in all common solvents, so surfactants and ultrasonication, which is known to cause structural damage and limits the length of dispersed SWNTs, are required for the preparation of solutions. In practice, the dispersed SWNTs are typically separated from amorphous carbon and other impurities present in the bulk samples by centrifugation, which also allows the separation of large agglomerates or bundles of SWNTs, the significance of which is discussed further below. A significant advance in the processing of solution-dispersed SWNTs has been the separation of SWNTs by their diameter and electronic type (metallic or semiconducting), which can be achieved using density gradient ultracentrifugation, based on the difference of densities of surfactant-wrapped metallic and semiconducting SWNTs, which are in turn caused by a difference in SWNT-surfactant interactions. Separation of metallic and semiconducting SWNTs has also been demonstrated using gel agarose chromatography, and semiconducting SWNTs can be selectively dispersed using conjugated polymers.

![Figure 2.3.3.](image.png) A transmission electron micrograph of SWNT bundles, collected from a floating catalyst CVD process on a holey carbon microscopy grid. Data courtesy of Aqeel Hussain.
The handling and properties of SWNTs are complicated by a ubiquitous phenomenon called bundling, or the formation of closely packed “ropes” or “bundles” of SWNTs, held together by the strong van der Waals forces between them. Interpreting the published literature on SWNTs and particularly thin films fabricated from them is complicated by the fact that in many publications, the degree of bundling is unknown and reported structural lengths may either refer to the constituent SWNTs, or the bundles formed by them. On the level of an individual SWNT, the dielectric screening caused by adjacent SWNTs in a bundle modulates the electronic properties, which can be observed as a redshift of the optical transitions, caused by decreased exciton lifetime. The screening of an external electric field, such as a gate bias, makes bundling a particular issue in the fabrication of field effect transistors, since the conductivity of bundles cannot be modulated efficiently. The screening by adjacent SWNTs may also lead to opening of small band gaps in metallic SWNTs. Radosavljevic et al. have reported that under low bias, conduction in bundles containing pathways of metallic SWNTs occurs in a limited number of SWNTs within the bundle and predominantly on the surface, which is directly contacted by external electrodes. Han and Strano have likewise reported that in bundles of purified semiconducting SWNTs, carrier scattering is greatly increased compared to single SWNTs. These findings indicate that conduction through a bundle cannot be simply assumed to correspond to conduction through its constituent SWNTs in parallel. The diameter \( d_b \) of a hexagonally packed bundle, as a function of the number of CNTs \( n \), is approximately

\[
d_b(n) \approx d_{CNT} \sqrt{n}. \tag{2.3.3}
\]

In Publication I, this relation is used to relate the bundle sizes predicted by aerosol measurements and measured by atomic force microscopy. The effects of bundling on SWNT thin film properties are discussed in more detail in Chapter 2.5. and in Publications I and III.

### 2.4 Electrical transport in single-walled carbon nanotubes

In quasi-one-dimensional structures, the electrical conductance and the probability of electron transmission through the structure are related by the Landauer formula, which in the case of a single, ideally contacted SWNT gives the conductance

\[
G = \frac{e^2}{h} \sum_i \Xi_i(E_F) = \frac{4e^2}{h} = 2G_0 = 155 \mu S, \tag{2.4.1}
\]

where \( \Xi_i(E_F) \) is the transmission of the \( i \)th sub-band at \( E = E_F \), \( G_0 \) is the conductance quantum and the factor of 2 results from the fact that two sub-bands intersect the \( K \) and \( K' \) points. In the case of non-ideal contacts and scattering in the SWNT, the resistance of an SWNT with length \( L_{SWNT} \) can be written as the sum

\[
R_{total} = \frac{h}{4e^2} + 2R_{contact} + \frac{h}{4e^2} \frac{l_{MFP}}{L_{SWNT}} \tag{2.4.2}
\]

where \( R_{contact} \) is the contact resistance to the SWNT and \( l_{MFP} \) is the electron mean free path in the SWNT. In practice, conductance values close to the quantized conductance given by Eq. 2.4.1. has been reached in both in cryogenic temperatures and at room temperature, but they are highly sensitive to the contacts and especially in the case of semiconducting SWNTs, the length of the SWNT segment forming the channel between the contacts. Transport through
the SWNT can be ballistic over micrometer lengths (corresponding to equally long mean free paths $l_{\text{MFP}}$) owing to the fact that the stiff $sp^2$ molecular structure results in a low optical phonon population at room temperature. At low biases, $l_{\text{MFP}}$ is ultimately limited by acoustic phonon scattering and at longer distances, transport along the SWNT becomes diffusive with observed Ohmic resistivities of approximately 4-6 kΩ/µm$^2$. At high biases and temperatures, the emission of optical phonons and backscattering limits the conductivity, as the electron energies approach the optical phonon energy $\hbar \omega_0 = 0.15$-0.2 eV. This causes the maximum current carrying capacity of a single SWNT to be approximately $(4e^2/\hbar)(\hbar \omega_0/e) \approx 25$ µA.$^6^4$

One or multiple semiconducting SWNTs can be used as the channel of a nanoscale field effect transistor (FET)$^{6^9-7^0}$. The high intrinsic charge carrier mobilities of semiconducting SWNTs, estimated to be in excess of 100000 cm$^2$/Vs at room temperature, and high measured field effect mobilities$^7^1$ make them a promising candidate material for future high-speed electronics. When measured by the energy-delay product, SWNT-based nanoscale FETs have been projected to outperform the currently used silicon-based FinFET technology at the future semiconductor process nodes of 7 nm and 5 nm$^7^2$, although for their practical application in integrated circuits, semiconducting SWNTs would need to be separated to extremely high purities (on the order of one parts per billion), placed at a consistent sub-10 nm pitch, and contacted well using a relatively short, ca. 10 nm contact length.

In contrast to conventional semiconductor engineering, where regions of doped semiconductors can be used as contacts, transport in SWNT FETs is complicated by the metal-SWNT interface. Fundamentally, electrical transport in SWNTs is ambipolar due to their band symmetry near the $K$ points. However, Schottky barriers formed at the interface between a metal and a semiconducting SWNT cause preferentially $p$- or $n$-type transport depending on the work function of the metal. High work function metals such as Au or Pd are expected to make preferentially $p$-type contacts, while low work function metals such as Al are expected to make $n$-type contacts, as reflected by the Schottky barrier heights for holes and electrons$^7^3$,

$$\phi_{B,\text{hole}} = \phi_{\text{CNT}} + \frac{E_g}{2} - \phi_M, \quad \phi_{B,\text{electron}} = \phi_M + \phi_{\text{CNT}} + \frac{E_g}{2},$$  \hspace{1cm} (2.4.2)

where $\phi_M$ is the work function of the metal (e.g. 5.1 eV for Au or Pd, 4.1 eV for Al), $\phi_{\text{CNT}}$ is the work function of the SWNT, and $E_g$ is the band gap of the SWNT. An illustration of a simple back-gated SWNT FET, its transfer curve and the band bending modulating transport through the Schottky barriers is shown in Figure 2.4.1. Ohmic $p$-type contacts to SWNTs can be achieved using high work function metals, most commonly palladium (Pd), but matching the work function is not sufficient in itself, since the junction geometry and in particular the wetting of SWNTs by the metal also affect the contacts. For example, gold (Au), while possessing an almost identical work function, does not wet SWNTs as well and forms comparably worse contacts than Pd. The situation is further complicated by the adsorption of atmospheric molecules such as H$_2$O or O$_2$ on the metal-SWNT interface, which typically causes an increase in the work function and thus moves the preference towards $p$-type transport. The sensitivity of a SWNT FET to ambient conditions may be utilized in chemical sensing, since transport through the FET is affected by the adsorption of even small amounts of molecules$^7^4$, and selectivity to certain species of gases or vapors may be increased by decorating the SWNT sidewalls$^7^5$ or non-covalently wrapping the SWNTs$^7^6$. Because the SWNT surface and contact interfaces are highly sensitive to absorbed molecules, non-passivated SWNT FETs and correspondingly,
thin film transistors discussed later, also show significant hysteresis in their transfer characteristics. The source of the hysteresis is understood to be charge traps in the dielectric-ambient interface, such as those caused by water molecules bound on SiO₂, and a passivation provided by the dielectric in top gate devices is normally sufficient to suppress this⁷⁷.

Controllable p- or n-type doping of the contacts has been reported using both organic⁷⁸-⁸⁰ and inorganic⁸¹ dopants, although the stability of both may not be suitable for practical fabrication of integrated circuits. Complementary logic has also been demonstrated by using low work function metals as source and drain contacts in the n-type FETs and high work function metals in the p-type FETs⁸². A promising approach for fabricating Ohmic contacts to SWNTs with short contact lengths are end-bonded contacts of e.g., molybdenum, which forms a carbide matching layer on the SWNT interface when heated to a sufficiently high temperature⁸³, and complementary logic has been demonstrated by combining end-bonded contacts of this type with a passivation layer that also acts as an n-type dopant⁸⁴.

At the moment of writing, no reproducible method of selectively growing semiconducting SWNTs with lengths suitable for device fabrication has been demonstrated, which necessitates the use of sorting or selective dispersion of SWNTs by electronic type, discussed in Chapter 2.3., or the selective post-fabrication removal of metallic SWNTs. Metallic SWNTs can be selectively destroyed after device fabrication using a straightforward electrical breakdown technique, originally demonstrated by Collins et al.⁸⁵ By reverse biasing a “leaky” SWNT FET with metallic SWNTs in the channel to quench electrical conduction through semiconducting SWNTs and simultaneously applying a high source-drain bias, metallic SWNTs will exceed their current carrying capacity and combust. With a suitable circuit design, the breakdown procedure can be applied simultaneously even in relatively complex integrated circuits⁸⁶-⁸⁷. In addition to breakdown by oxidation in ambient conditions, similar techniques can be applied to selectively pattern an etching mask on top of the SWNTs by means of thermocapillary flows in a polymer⁸⁸, or the sublimation of an organometallic layer⁸⁹, induced by heating, and the exposed metallic SWNTs can be subsequently removed by reactive plasma etching.

As mentioned earlier, practical application of SWNT-based FETs in integrated circuits require the placement of parallel SWNTs at a small, consistent pitch, since the drive currents achievable using single SWNTs are not sufficient for high performance integrated circuits and variations in SWNT density lead to unacceptable variation in device properties. Aligned arrays of SWNTs can be prepared by surface CVD growth from catalyst stripes patterned on a sapphire substrate, as mentioned in Chapter 2.3., or from sorted liquid dispersions using the Langmuir-
Schaefer method\textsuperscript{90}, alternating current dielectrophoresis\textsuperscript{91}, or evaporative self-assembly\textsuperscript{92}. At the moment of writing, combining a high and consistent SWNT density with good electrical contacts to the SWNTs remains a challenge, with most studies of parallel, dense SWNT arrays obtaining ON-state conductances far less than the ideal value of $2G_0$ per SWNT. At the moment of writing, the record conductance for such devices is approximately $0.46G_0$ per SWNT, obtained at an SWNT pitch of ca. 21 nm and micrometer-scale contacts\textsuperscript{92}.

The use of thin films of SWNTs as the channel material in thin film transistors (TFTs), where the source and drain distance is typically larger than the length of an individual SWNT is discussed in Chapter 2.5. The electrical properties of thin films of SWNTs are largely determined by electrical transport across SWNT-to-SWNT junctions. Based on two- and three-terminal measurements of crossed SWNTs\textsuperscript{71} and conducting atomic force microscopy\textsuperscript{93}, junctions between metallic SWNTs, semiconducting SWNTs with similar bandgaps and bundles of mixed SWNTs have been observed to essentially operate as tunneling junctions with low-bias resistances of tens or hundreds of kΩ. Meanwhile, Schottky barriers similar to those in the interfaces between semiconducting SWNTs and metals, and associated depletion regions in the semiconducting SWNTs\textsuperscript{71}, are formed in junctions between metallic and semiconducting SWNTs. The transmission probabilities over such junctions and the resulting resistances are also dependent on the junction geometry and elongated Y-shaped junctions with larger contact areas generally show lower resistances\textsuperscript{93}.

2.5 Thin films of single-walled carbon nanotubes

Random, partially aligned or aligned thin films of SWNTs, occasionally called “buckypapers” in reference to the paper-like microstructure of random thin films and the C\textsubscript{60} buckminsterfullerene structure, are an attractive material for a wide range of applications, such as thin conducting films (TCFs) and thin film transistors (TFT). While the electrical and thermal conductivity of the thin films are several orders of magnitude lower than the intrinsic properties of their constituent SWNTs due to SWNT-to-SWNT contacts, they are still high enough for many applications. In contrast to conventional metal or metal oxide thin films, SWNT films maintain their properties extremely well under repeated mechanical flexing or stretching, making them suitable for the fabrication of large-area electronics on flexible and stretchable substrates\textsuperscript{81}. A photograph of a transparent (ca. 96% transmittance at visible wavelengths) and conductive (a sheet resistance of ca. 200 Ω/sq.) SWNT coating on 100 μm thick poly(ethylene terephthalate) (PET) sheet, and a scanning electron micrograph of the structure of a similar film are shown in Figure 2.5.1.
SWNT thin films can be fabricated by a large variety of methods. Liquid-dispersed SWNTs can be deposited into thin films using e.g. vacuum filtration\(^{94}\), dip coating\(^{95}\), spray coating\(^{96}\), transfer printing\(^{97}\), Langmuir-Blodgett assembly\(^{98}\), inkjet and aerosol jet printing\(^{94,99}\) and numerous other methods. As mentioned in Chapter 2.3, thin films can be easily fabricated using SWNTs grown by the FCCVD synthesis process by collecting the SWNTs on a filter and transferring the film on a target substrate by pressing the filter on it, if the SWNT film is thick enough to form an interlinked, self-supporting structure\(^{46}\). Alternatively, the filter may be dissolved to transfer the SWNT film\(^{100}\).

Depending on its constituent SWNTs and density, the electrical properties of an SWNT thin film may be either as metallic or semiconducting. When the film consists of a mixture of semiconducting and metallic SWNTs, the behavior is determined by the SWNT dimensions and density according to percolation theory. In an infinite two-dimensional system of line segments, placed randomly at a density \(N\), a continuous network of intersecting line segments is formed at the critical density \(N_c\) determined by

\[
N_c \langle l^2 \rangle = 5.63726, \quad (2.5.1)
\]

where \(\langle l \rangle\) is the expectation value of the line segment length\(^{101-102}\). If the film consists of a typical unprocessed SWNT mixture, in which approximately two thirds of the SWNTs are semiconducting, Eq. 2.5.1 gives the critical density for a mixed pathway of metallic and semiconducting SWNTs and the corresponding critical densities for pathways formed along pure semiconducting or purely metallic SWNTs are 1.5 and 3 times higher. In a thin film containing only mixed or semiconducting pathways, conductance can be modulated using a gate voltage even without the removal of metallic SWNTs, because each available pathway from the source to the drain will contain contacts between semiconducting and semiconducting SWNTs, contacts between metallic and semiconducting SWNTs, or contacts between the source/drain electrode and a semiconducting SWNT. The net conductance of the channel can be then controlled by a gate bias or chemical doping\(^7\). Snow et al. first demonstrated the possibility to use random, low-density (approximately or less than 1 SWNT/\(\mu m^2\)) networks of unsorted SWNTs as an electronic material\(^{103}\), and in parallel to the development of FETs in which the channel consists
of single SWNT or a parallel array of SWNTs, SWNT thin film transistors (TFTs) have been considered for large-area electronics such as touch screen and display drivers. Due to the mechanical robustness of SWNT thin films, they are also promising as a material for inexpensive flexible electronics manufactured using printing techniques. Prior to Publications II-IV, Sun et al.\textsuperscript{100} have demonstrated the fabrication of thin film transistors and small integrated circuits (logic gates and ring oscillators) on Si/SiO\textsubscript{2} and polymer substrates using unsorted SWNTs synthesized using the FCCVD process, and also demonstrated that such TFTs withstand stretching and molding by thermoforming, when their contact electrodes and interconnects are fabricated from a thick, metallic SWNT film\textsuperscript{104}. The achievable ON-state current in devices containing mixed pathways is severely constrained by the SWNT densities that can be used, and the devices reported in Publication IV probably approach the maximum values obtainable without enrichment of semiconducting SWNTs.

For practical applications, semiconductor enriched SWNTs are thus needed, but the geometry of the TFT channel and the lower scales of integration in many of the intended applications mean that lower purities could be used compared to the SWNT FET based microelectronics discussed earlier. Components such as static random access memory (SRAM)\textsuperscript{105}, active matrix backplanes for organic light emitting diode (OLED) displays\textsuperscript{106} and tactile sensors\textsuperscript{107}, and flexible TFTs with an intrinsic cutoff frequency of 170 MHz\textsuperscript{108}, sufficient for e.g. radio frequency identification, have been demonstrated using ca. 99% semiconducting SWNT solutions, which are available commercially or can be produced in academic facilities.

![Figure 2.5.2. Numerically simulated probabilities of forming a percolating cluster of mixed, purely semiconducting and purely metallic SWNTs, modelled as line segments, in a 50 x 50 \( \mu \text{m} \) device. The lengths of SWNTs are sampled from a log-normal distribution with a mean of 3 \( \mu \text{m} \) and a variance of 0.5 \( \mu \text{m} \) and their orientations are isotropic. The vertical dashed lines are predictions from Eq. 2.5.1.](image)

An attractive feature of SWNT TFTs, increasing their applicability in printed electronics where thick polymer dielectrics are commonly used, is the increased capacitance coupling between the SWNT channel and the gate. The use of thick dielectrics usually leads to higher operating voltages (tens of volts) in silicon-based and organic TFTs, because the gate-channel capacitance decreases in proportion to the inverse of the gate insulator thickness in a planar channel. However, in SWNT thin films, where the spacing between the CNTs can be large compared with the thickness of the gate insulator, the electrostatic coupling between the nanotubes and the gate electrode is enhanced by electric field line focusing on the nanotubes, whose diameters are in the order of nanometers\textsuperscript{109}. Consequently, the gate-to-channel capacitance scales as a function of \( \log^{-1}(t) \), where \( t \) is the gate insulator thickness, leading to comparably higher gate-channel capacitances.
Cao et al.\textsuperscript{109} have proposed an analytical expression for the gate-channel capacitance taking into account the field line focusing,

\begin{equation}
C = \Lambda_0^{-1} \left[ C_Q^{-1} + \frac{1}{2\pi \varepsilon} \ln \left( \frac{\Lambda_0}{\pi R} \right) \sinh \left( \frac{2\pi d}{\Lambda_0} \right) \right]^{-1}, \tag{2.5.2}
\end{equation}

where \(\Lambda_0\) is the linear spacing between SWNTs, \(R\) is the radius of the SWNT, \(d\) is the dielectric thickness, and \(C_Q\) is the quantum capacitance of a SWNT. The use of Eq. 2.5.2. may overestimate the capacitance, and direct capacitance-voltage measurements of SWNT TFT channels tend to measure capacitances above and the corresponding capacitance of a parallel plate capacitor, \(C = \frac{\varepsilon}{4\pi d}\). In particular, the sensitivity of Eq. 2.5.2 to variation in \(\Lambda_0\) should be noted.

Thicker SWNT films with metallic properties have applications particularly as transparent conducting films (TCFs), or conducting layers of material that simultaneously have a high electrical conductivity and transmittance at visible wavelengths, used in e.g. thin film and touch displays and photovoltaic devices\textsuperscript{46, 94, 111} The performance of a TCF is normally indicated by a combination of its transmittance at optical wavelengths (commonly 550 nm) and sheet resistance, and the practical requirements for those vary significantly by the intended application. For example, touch sensing elements can be fabricated even from less conductive TCFs with sheet resistances of ca. 500 \(\Omega/\text{sq.}\) at 85-90\% transmittance, whereas in photovoltaic devices, the electrodes should ideally be as conductive as possible to maximize the efficiency of energy harvesting\textsuperscript{10}.

A schematic and an example of a capacitive touch sensor display, similar to those found in consumer electronics at the moment of writing, is shown in Figure 2.5.4. Briefly, the sensor works by measuring the mutual capacitance between two intersecting TCF traces separated by an insulator, with each intersection working as a sensing element.
At the moment of writing, the most commonly used TCFs are doped metal oxides, most commonly indium-doped tin oxide (ITO), capable of reaching sheet resistances between 10 and 100 $\Omega$/sq. at over 85% visible transmittance, depending on the substrate and the quality of the material. These materials have a number of drawbacks: they contain expensive metals such as indium, which is susceptible to price fluctuations, their brittle ceramic structure cannot withstand strain or cyclic bending, they suffer from performance degradation due to corrosion of the material, and their deposition typically requires vacuum processing steps\(^{10}\). In addition to SWNTs, conducting polymers, metal nanowires and microstructures and graphene have been considered as replacements for ITO, although conducting polymers also suffer from degradation of performance, metal nanowires and grids are typically fabricated from expensive noble metals and suffer from optical haze, and graphene requires the transfer of multiple layers to reach low sheet resistances needed in most applications, with each consecutive transfer introducing contamination and defects\(^{10}\). As mentioned earlier, an advantage of the FCCVD method is that the effluent of the reactor can be collected by filtration or other aerosol sampling methods without further dispersion steps, and the SWNT thin film formed on a filter is mechanically robust and can be transferred on glass and polymer substrates by pressing the film on the substrate. Using this procedure, Kaskela et al.\(^{46}\) were able to fabricate TCFs with performance approaching commercial ITO on polymer substrates, or 110 $\Omega$/sq. after doping by nitric acid. Nasibulin et al. also demonstrated that SWNT films formed from longer bundles can be also transferred on substrates with openings to form free-standing films\(^{111}\), and reached a sheet resistance of 84 $\Omega$/sq. at 90% using doping by gaseous nitric oxide ($\text{NO}_2$). Kaskela et al.\(^{46}\) also introduced a straightforward figure of merit for comparing the performance of different TCFs,

$$K = \frac{\sigma_x}{A} = -\frac{1}{R_s \ln T} \quad (2.5.3)$$

where $\sigma_x$ is the reciprocal of the sheet resistance $R_s = -\ln T$ is the optical absorbance based on the Beer-Lambert law\(^*,\) $A = -\ln T$ is the transmittance of the film, typically measured at the reference wavelength of 550 nm. A comparison of SWNT-based TCFs fabricated using the FCCVD process, selected high performance SWNT TCFs fabricated using methods based on liquid dispersions and the results obtained in Publications III and V is shown in Table 2.5.1.

\(*\) In analytical chemistry, the Beer-Lambert law, and the corresponding absorbance, are usually expressed using the common logarithm, i.e. $A = -\log_{10} T$. To maintain consistency with Kaskela et al., the natural logarithm is used here. See also Corrigendum for Publication I.
Additional methods and the TCF performances obtained using them are covered e.g. in a review by Yu et al.\textsuperscript{10}.

In the literature, another figure of merit, derived originally for thin films of metals and based on the ratio of the film conductivity at optical wavelengths and DC conductivity, has been widely used after being originally applied to SWNT TCFs by Hu et al.\textsuperscript{112}:

\[
T = \left( 1 + \frac{Z_0 \sigma_{DP}}{2 \sigma_{DC}} \right)^{-2}, \tag{2.5.4}
\]

where \(Z_0 \approx 376.73 \, \Omega\) is the impedance of free space, and values of \(\sigma_{DP} = 150 \, \text{S} \) or \(200 \, \text{S}\) in the visible spectrum are commonly used. The ratio \(\sigma_{DP}/\sigma_{DC}\) is used as the figure of merit.

The conductivity of TCFs consisting of mixed metallic and semiconducting SWNTs is commonly improved by chemical doping, allowing the semiconducting SWNTs to contribute to the film conductivity and decreasing the contact resistances between SWNTs. The use of a large number of especially p-type dopants has been reported in the literature, but in principle they share the same of mechanism of operation that physisorption of the dopant compound leads to a downshift of the Fermi level, which in turn increases the charge carrier density in the SWNTs and reduces the height of the Schottky barriers between them. For example, in the case of nitric acid (HNO\textsubscript{3}), a commonly used dopant, Fermi level downshifts of 0.2 eV, based on X-ray photoelectron spectroscopy\textsuperscript{113}, and 0.35 eV, based a combination of transport measurements and optical spectroscopy\textsuperscript{114}, have been reported. Depending on the SWNTs and dopants used, the sheet resistance of a TCF an be typically reduced by factors of 3 to 8\textsuperscript{10}. In the case of surfactant-dispersed SWNTs, inorganic acids, which are commonly used as dopants, may also improve the TCF performance by removing surfactant remains.

As discussed in Chapter 2.3., at room temperature, the conductivity of longer SWNTs is typically Ohmic, with resistivities of 4-6 k\(\Omega/\mu\text{m}\) based on transport measurements of long SWNTs\textsuperscript{68, 115} and conductive atomic force microscopy along individual SWNTs and small bundles\textsuperscript{93}. Since the contact resistances between individual SWNTs are orders of magnitude higher\textsuperscript{60, 71, 93, 116}, tens or hundreds of k\(\Omega_s\), electrical conduction through an SWNT TCF is assumed to be limited by the contacts between SWNTs or bundles.

In addition to the nanotube or bundle length, the mean bundle size is expected to have an effect on the resulting thin film performance. Prior to Publications I and III, Hecht et al.\textsuperscript{117} and Shin et al.\textsuperscript{118} studied the performance of films fabricated by vacuum filtration of SWNT dispersions, and the bundle length and size were controlled by using different ultrasonication times. Hecht et al. could not make conclusions about the dependence between the bundle size and thin film performance, because decreasing the bundle size also decreased the bundle length in their experimental procedure, whereas Shin et al. claimed to be able to keep the bundle size and length less correlated, and concluded that the TCF performance is improved as the bundle size is decreased, for bundles of similar length. Lyons et al.\textsuperscript{119} and Mustonen et al.\textsuperscript{120} also considered the effect of bundling from a geometric viewpoint, using different commercially available SWNT dispersions and SWNTs synthesized using different FCCVD processes, respectively. They argued independently that decreasing the bundle diameter while keeping the optical density constant increases the number of conductive pathways in the network, and as a result, the bulk electrical conductivity. However, this could be counteracted if the conductivity of junctions between bundles increases proportionally to the bundle size, which can be expected due to larger contact areas. This has been experimentally observed using conductive atomic force microscopy by Znidarsic et al.\textsuperscript{93}, although an earlier study by Nirmalraj et al.\textsuperscript{60}
reached the opposite conclusion, possibly because their work used SWNTs deposited from a liquid dispersion, and larger bundles could contain more contaminants.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Process description</th>
<th>$R_s$ (Ω/sq.)</th>
<th>$T$ (%) at 550 nm</th>
<th>$K$ (kΩ⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu *et al.*⁹⁴</td>
<td>Filtering of SWNT solution and dissolution of filter, HNO₃ doping</td>
<td>30</td>
<td>80</td>
<td>149.4</td>
</tr>
<tr>
<td>Ostfeld *et al.*⁹⁶</td>
<td>Spray coating with SWNT solution, HNO₃ doping</td>
<td>150</td>
<td>90</td>
<td>63.3</td>
</tr>
<tr>
<td>Nasibulin *et al.*¹¹¹</td>
<td>Filtering of FCCVD effluent and press transfer, NO₂ doping</td>
<td>84</td>
<td>90</td>
<td>113</td>
</tr>
<tr>
<td>Mirri *et al.*⁹⁵</td>
<td>Dispersion in chlorosulfonic acid and dip coating</td>
<td>100</td>
<td>90</td>
<td>94.9</td>
</tr>
<tr>
<td>Hecht *et al.*¹²¹</td>
<td>Dispersion in chlorosulfonic acid, filtration and detachment from filter by a wet process</td>
<td>60</td>
<td>90.9</td>
<td>174.7</td>
</tr>
<tr>
<td>Mustonen *et al.*⁴⁵</td>
<td>Filtering from low concentration FCCVD process and press transfer, HNO₃ doping</td>
<td>63</td>
<td>90</td>
<td>150</td>
</tr>
<tr>
<td>Anoshkin *et al.*¹²²</td>
<td>Filtering from FCCVD process with mixed CO and ethylene feedstock, and press transfer, AuCl₃ doping</td>
<td>73</td>
<td>90</td>
<td>130</td>
</tr>
<tr>
<td><strong>Publication III</strong></td>
<td>Filtering from low concentration FCCVD process and press transfer, HNO₃ doping</td>
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<td>90</td>
<td>106.6</td>
</tr>
<tr>
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<td>Thermophoretic deposition from FCCVD process, AuCl₃ doping</td>
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<td>128.1</td>
</tr>
<tr>
<td><strong>Publication I</strong></td>
<td>Extrapolated optimum performance of an all-metallic network</td>
<td>25</td>
<td>90</td>
<td>379.6</td>
</tr>
</tbody>
</table>

*Table 2.5.1. A comparison on selected high performance SWNT-based TCFs and the results of Publications I, III, and V. For brevity, only values with $T$ close to 90% are reported.*
3. Aerosol transport and dynamics

3.1 Definitions

An aerosol is defined as solid particles or liquid droplets suspended in a gas. The sizes of aerosol particles range from single-nanometer molecular clusters to visible microscopic droplets and dust particles, and several of the physical models of aerosol dynamics discussed here are conceptually valid only for certain sizes of particles. The particle size regime is commonly described using the Knudsen number $Kn = 2\lambda/d_p$, where $\lambda$ is the mean free path of the gas molecules, or the average distance travelled between molecular collisions, and $d_p$ is the diameter of the particle. In air or nitrogen at ambient conditions, $\lambda$ is approximately 65 nm, and can be calculated from the gas properties using

$$\lambda = \frac{m_g}{\sqrt{2\pi \rho_g \sigma^2}}$$  \hspace{1cm} (3.1.1)

where $m_g$ is the mass of the gas molecule, $\rho_g$ is the volumetric density of the gas, and $\sigma$ is the kinetic diameter of the gas molecule.

In the free molecular regime, or when $Kn > 1$, the particle size is on the same order of magnitude as the mean free path of the gas molecules, and the interactions between the surrounding gas and the particles can be described using the kinetic theory of gases. In the continuum regime, where $Kn < 1$, the diameter of the particle $d_p$ is much larger than $\lambda$ and the behavior can be described by the continuum models of fluid dynamics, diffusion and heat transfer. The size range between these two cases is referred to as the transition regime. Phenomena in the transition regime are usually described by semiempirical formulae based on interpolation between the free molecular and continuum cases.

3.2 Diffusive transport

Aerosol particles are small enough to undergo significant Brownian motion, the strength of which is strongly dependent on the particle size and is expressed by the diffusion coefficient or diffusivity $D$. In one dimension, the concentration of particles with number size concentration (number of particles per volume) $n$, initially at $x = 0$, evolves in time according to the diffusion equation, or Fick's second law,

$$\frac{dn}{dt} = D \frac{d^2 n}{dx^2}$$  \hspace{1cm} (3.2.1)

The solution of Eq. 3.2.1. is
$n(x,t) = \frac{N_0}{\sqrt{4\pi D t}} \exp \left( \frac{-(x^2)}{4Dt} \right), \quad (3.2.2)$

where $N_0$ is the initial number concentration of the particles at $x = 0$. The mean square displacement of a particle at time $t$, relative to an initial coordinate $x = 0$ is

$$\bar{x}^2 = \frac{1}{N_0} \int_{-\infty}^{\infty} x^2 n(x,t) dx, \quad (3.2.3)$$

which, after inserting Eq. 3.2.2, gives

$$\bar{x}^2 = 2Dt. \quad (3.2.4)$$

The diffusion constant $D$ can be thus interpreted physically as the proportionality of the mean square displacement and time.

In an aerosol where the number concentration of aerosol particles per unit volume $n$ is non-uniform, collisions caused by Brownian motion lead to a collective motion of particles from regions of higher concentration to regions of lower concentration. The flux of particles $J$, expressed in particles moving through a unit area, is given by Fick’s first law,

$$J = -D \frac{dn}{dx} \quad (3.2.5)$$

Sutherland and Einstein independently derived an expression for $D$ using the equipartition principle. Briefly, they postulated that in equilibrium, the kinetic energy of a system should be proportional to the thermal energy $k_B T$, where $k_B$ is Boltzmann’s constant and $T$ is the temperature, resulting in a diffusion constant of the form

$$D = \frac{k_B T}{F/v}, \quad (3.2.6)$$

where $F/v$ is the ratio between an arbitrary frictional force hindering the movement of the diffusing particle and the terminal velocity of the particle. In the case of particles moving in a fluid and following Stokes’ continuum law for the drag force

$$F_D = 3\pi \mu_g d_p v \quad (3.2.7)$$

where $\mu_g$ is the dynamic viscosity of the gas, $v$ is the velocity of the moving particle, and $d_p$ is the particle diameter, Eq. 3.2.6 results in

$$D = \frac{k_B T}{3\pi \mu_g d_p} \quad (3.2.8)$$

Stokes’ law for the drag force is based on the assumption, valid in the continuum regime, that the velocity of the surrounding gas goes to zero at the surface of the moving body. An empirical correction called the Cunningham slip correction factor $C_c$ can be used to extend the validity of Stokes’ law to the transition and the free molecular regimes. At standard pressure, $C_c$ is given by the semiempirical equation:\textsuperscript{13}
\[ C_c = 1 + \frac{x}{d_p} \left( 2.514 + 0.8 \exp \left( -0.55 \frac{d_p}{\lambda} \right) \right) \]  \hspace{1cm} (3.2.9)

where the three numerical constants have been determined empirically. Depending on the source, the specific values of these numerical constants may also vary slightly. Slip-corrected values for the drag force and diffusion constant can be obtained by dividing Eq. 3.2.7. and multiplying Eq. 3.2.8. by \( C_c \).

In the free molecular regime, the drag force acting on a spherical particle, moving slowly compared to the movement of the gas molecules surrounding, follows from the kinetic theory of gases. In the case where the particle is small enough that the velocity distribution of the surrounding gas molecules follows the Maxwell-Boltzmann velocity distribution:

\[ f_v(v) = \frac{m}{2\pi k_B T} \frac{1}{\sqrt{2\pi k_B T}} \exp \left( -\frac{m v^2}{2k_B T} \right) \]  \hspace{1cm} (3.2.10)

the net momentum transfer caused by collisions between the particle and the surrounding gas results, according to Epstein \(^{124}\), in the drag force:

\[ F_D = \frac{2}{3} d_p^2 \rho_g \sqrt{\frac{2\pi k_B T}{m_g}} \left( 1 + \frac{\pi \alpha}{8} \right) v, \]  \hspace{1cm} (3.2.11)

where \( \alpha \) is the momentum accommodation factor, or proportion of diffuse to specular scattering on the particle surface, and \( \rho_g \) is the density of the gas.

Physically, the momentum accommodation factor \( \alpha \) accounts for different transfers of momenta in the cases of specular scattering, where the inbound gas molecule collides with the surface elastically, and diffuse scattering, where the gas molecule reaches thermal equilibrium with the surface and departs at a random velocity determined by the Maxwell-Boltzmann velocity distribution. In practice, \( \alpha \) is typically assumed to be 0.9 based on the Millikan oil drop experiments \(^{14}\), indicating that a majority of collisions the typically diffusive.

Several authors have published generalized versions of the free molecular regime drag force, or Eq. 3.2.11, which account for the intermolecular forces between the particle surface and the gas molecules and a momentum accommodation factor \( \alpha \) dependent on the particle size. These are further discussed in Ch. 3.3 due to their significance to the thermophoretic transport of nanoscale particles.

The transport and measurement of nanoparticle aerosols are complicated by the fact that their high diffusivity leads to diffusive deposition on e.g. the walls of flow channels. The specific rate of deposition depends on the channel geometry and flow regime, and empirical models are available for common cases. In the case of laminar flow through a tube with a circular cross-section, a set of empirical equations is given in Hinds \(^{13}\):

\[
\frac{n_{au}}{n_{in}} = 1 - 5.5 \left( \frac{DL}{Q} \right)^2 + 3.77 \left( \frac{DL}{Q} \right), \text{ when } \left( \frac{DL}{Q} \right) < 0.007,
\]

\[
\frac{n_{au}}{n_{in}} = 0.819 \exp \left( -11.5 \frac{DL}{Q} \right) + 0.0975 \exp \left( -70.1 \frac{DL}{Q} \right) + 0.0325 \exp \left( -179 \frac{DL}{Q} \right), \text{ when } \left( \frac{DL}{Q} \right) > 0.007, \]  \hspace{1cm} (3.2.12)

where \( L \) is the length of the tube and \( Q \) is the volume flow rate through the tube. As an illustrative example, the purely diffusive loss, when nanoparticles with \( d_p = 3 \text{ nm} \) are carried
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through in a 1-meter tube in a 0.5 l/min volumetric flow of nitrogen at room temperature, is approximately 58%.

Figure 3.2.1. A depiction of specular scattering and diffuse scattering of gas molecules from a particle surface. In specular scattering (upper graphic) the gas molecule undergoes an elastic collision with the surface and ... In diffuse scattering, the velocity of the gas molecule after collision is random and determined by the Maxwell-Boltzmann velocity distribution (Eq. 3.2.1) at the temperature of the particle. The momentum accommodation factor $\alpha$ indicates the proportion of diffuse to specular scattering events on the surface.

The diffusive transport of non-spherical aerosol particles can be described using the treatment for spherical particles, corrected by a shape factor dependent on the shape and aspect ratio of the non-spherical particle, and high aspect ratio particles such as SWNTs and MWNTs are normally treated as ellipsoids or cylinders. A summary of these corrections and models has been published by Kulkarni et al.\textsuperscript{125}, and some of them, particularly those concerning fractal-shaped agglomerates, are covered in a review by Mädler and Friedlander\textsuperscript{126}. The translational diffusion of fiber-shaped aerosol particles has been a topic of active study particularly because diffusive transport is a major contributor to their deposition in the smaller airways and alveoli of human lungs\textsuperscript{127}. Outside of \textbf{Publication I}, experimental data on the diffusive transport of SWNTs and small SWNT bundles is very limited, probably because aerosolizing SWNTs from liquid dispersions is highly challenging, and the models have not been experimentally verified using aerosols of similar diameters and aspect ratios.

3.3 Diffusive agglomeration

When colliding solid aerosol particles stick to each other, they form agglomerates or various shapes, and liquid droplets can similarly coagulate into larger droplets. In the context of FCCVD synthesis of SWNTs, bundling during the synthesis process, studied in \textbf{Publications I and III}, can be also seen as a specific case of agglomeration. The problem of aerosol agglomeration was first studied by Smoluchowski, who described the temporal evolution of the number concentration of an aerosol species (which can mean e.g. the droplet size or the size of an agglomerate, expressed in number of primary particles) in an aerosol undergoing agglomeration using a population balance equation\textsuperscript{128}. A process in which two particle species $i$ and $j$ (with number concentrations $n_i$ and $n_j$ and particle volumes $v_i$ and $v_j$) collide to form agglomerates of species $k$ (with number concentration $n_k$ and volume $v_k = v_i + v_j$) at a collision
rate determined by an agglomeration kernel $K_{ij}(v_i, v_j, T, P, ... )n_in_j$, dependent on the properties (typically the size) of the particle species $i$ and $j$ and the physical mechanism causing the collisions, results in a population equation for $n_k$

$$
\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} n_i n_j - \sum_{i=1}^{\infty} K_{ik} n_i n_k,
$$

(3.3.1)

where the first term describes the rate of formation of $k$ due to collisions between $i$ and $j$, and the sum is over pairs $(i,j)$ for which $i + j = k$, and the second term describes losses of $k$ due to collisions with other species of particles, and the sum is over all species of particles under consideration. A graphical depiction of Eq. 3.3.1 in the case where the aerosol species are agglomerates of solid particles is shown in Figure 3.3.1a.

![Figure 3.3.1.](image)

**Figure 3.3.1.** a) A graphical representation of the Smoluchowski population equation (Eq. 3.3.1), in a case where the different aerosol species correspond to solid agglomerates of 1 to $n$ primary particles. The upper part describes the formation of a species $k$ corresponding to four primary particles, or the first sum in Eq. 3.3.1. The lower part describes the loss of $k$ due to collisions with other species $i$, where $i$ runs over all species considered, or the second sum in Eq. 3.3.1. b) A depiction of the system considered in Eqs. 3.3.2 – 3.3.9.

In the original treatise of Smoluchowski, the agglomeration kernel $K_{ij}$ is derived for a system in which collisions are caused by diffusive transport. One can consider a spherically symmetric system, where a stationary spherical particle of species $i$, with radius $r_i$, is set at $r = 0$ and surrounded by diffusing particles of species $j$, with radii $r_j$ and number concentration $n$, and collisions due to Brownian diffusion are the only source of agglomeration. For simplicity, it can be assumed that the stationary particle is a perfect sink for the diffusing particles, which stop when they collide with its surface at $r = r_i + r_j$. A sketch of this system is given in Figure 3.3.1b. Based on Eq. 3.2.1, the diffusion rate of the moving particles is

$$
\frac{dn}{dr} = D \left( \frac{\partial^2 n}{\partial r^2} + \frac{2}{r} \frac{\partial n}{\partial r} \right),
$$

(3.3.2)

with the boundary conditions $n = 0$ when $r = r_i + r_j$ (indicating that the number concentration of freely diffusing particles $j$ goes to zero at the surface of the stationary particle) and $n = n_0$ when $t = 0$ or when $r \gg r_i + r_j$ (indicating that the initial number concentration of $j$ is $n_0$, and
remains so far away from the surface of the stationary particle). The solution of Eq. 3.2.11 is given by

\[
\frac{n-n_0}{n_0} = - \frac{r_i-r_j}{r} \left( 1 - \text{erf} \left( \frac{r-(r_i+r_j)}{2\sqrt{D}} \right) \right),
\]  
(3.3.3)

where \( \text{erf} \) is the error function. According to Eq. 3.2.5, the total particle flux on the surface of the fixed particle \((r = r_i + r_j)\), equivalent to the collision rate \( K_{ij} \), is

\[
I = J A = 4\pi r^2 D \frac{dn}{dr},
\]
(3.3.4)

where \( J = D \frac{dn}{dr} \) is the unit flux per surface. By calculating \( \frac{dn}{dr} \) based on Eq. 3.3.2, Eq. 3.3.3 can be rewritten as

\[
I = 4\pi D (r_i + r_j) n_0 \left( 1 + \frac{(r_i+r_j)}{\sqrt{8D}} \right).
\]
(3.3.5)

In the steady state limit of \( t \gg (r_i + r_j)^2/D \) the last term vanishes, so

\[
I = K_{ij} = 4\pi D (r_i + r_j) n_0.
\]
(3.3.6)

Additionally, it should be taken into account that particles of species \( i \) are also undergoing diffusion. The relative diffusivity of two particles undergoing diffusive movement independently with respect to each other is given by the Einstein relation: By denoting the displacements of the particles by \( x_i, x_j \), the relative diffusion constant \( D_{ij} \) is given by

\[
D_{ij} = \frac{(x_i-x_j)^2}{2t} = \frac{x_i^2}{2t} + \frac{x_j^2}{2t} + \frac{x_i x_j}{2t} = \frac{x_i^2}{2t} + \frac{x_j^2}{2t} = D_i + D_j,
\]
(3.3.7)

where \( \langle x_i x_j \rangle = 0 \) when the movement of the particles is uncorrelated, as assumed above. Eq. 3.3.5 can then be rewritten as

\[
K_{ij} = 4\pi (D_i + D_j) (r_i + r_j).
\]
(3.3.8)

Using Eq. 3.2.8, the agglomeration kernel given by Eq. 3.3.8 can be written in terms of the volumes of spherical particles as

\[
K_{ij} \left( v_i, v_j \right) = \frac{2k_BT}{3\mu_g} \left( \frac{1}{v_i^{1/3}} + \frac{1}{v_j^{1/3}} \right) \left( v_i^{1/3} + v_j^{1/3} \right).
\]
(3.3.9)

A similar relation can be derived using the drag force in the free molecular regime, or Eq. 3.2.11. In the case of nontrivial agglomeration kernels, the Smoluchowski population equation with cannot be solved analytically, so numerical methods or approximations are used in practice instead. In **Publication I**, the evolution of the size and number concentration of an SWNT aerosol is studied using the monodisperse approximation, in which the agglomerating aerosol is assumed to consist of a single species \( i \), and the agglomeration kernel \( K_{ij} \) is assumed to be constant over the whole aerosol and time considered. Although the assumptions of the monodisperse approximation are relatively rough, it has been successfully used to qualitatively
predict the evolution of the total number concentration and average particle size in a number of systems.\textsuperscript{13} The same approach is used to justify the results of \textbf{Publication III}. By setting $v_i = v_j$, Eq. 3.3.9 simplifies to $K_{ij} = K = \frac{8k_BT}{3\mu_g}$. In a system of monodisperse, indistinguishable particles, Eq. 3.3.1 can be rewritten using the total number concentration $\sum_{i=1}^{\infty} n_i = N$ as

$$\frac{dN}{dt} = \frac{1}{2} K \sum_{i}^{\infty} \sum_{i+i} n_i n_i - K \sum_{i}^{\infty} \sum_{i}^{n} n_i n_i = -\frac{K}{2} N^2 = -K_{\phi} N^2, \quad (3.3.10)$$

where the first term in principle amounts to that for each collision between two particles, a new particle of the same species is created, the second term amounts to that the original particles are removed, and $K_{\phi} = \frac{K}{2} = \frac{4k_BT}{3\eta}$. Because the mobility diameters considered in \textbf{Publication I} are in the sub-micrometer range, the Cunningham slip correction factor $C_c$ given by Eq. 3.2.9 can be applied to extend the validity of Eq. 3.3.9., resulting in the monodisperse aggregation coefficient

$$K_{\phi} = \frac{4k_BT C_c}{3\mu_g}. \quad (3.3.11)$$

Solving Eq. 3.3.10 for $N(t)$ gives

$$N(t) = \frac{N_0}{1 + N_0 K_{\phi} t}, \quad (3.3.12)$$

where $N_0 = N(t = 0)$ is the initial number concentration.

Assuming no other loss mechanisms except agglomeration, the average number of particles per agglomerate $n_p$ grows as

$$n_p(t) = n_{p0} + \frac{N_0}{N(t)} - 1 = n_{p0} + N_0 K_{\phi} t, \quad (3.3.13)$$

where $n_{p0} = n_p(t = 0)$ is the initial particle size. In \textbf{Publication I}, Eq. 3.3.13, combined with the bundle diameter given by Eq. 2.3.3, is used to predict the increase in bundle size in an agglomerating SWNT aerosol.

### 3.4 Thermophoretic transport

Thermophoresis, or the movement of aerosol particles by a temperature gradient, was first described by Tyndall, who reported that when dusty or smoky air was blown across a heated wire, a zone of dust-free air was created in the immediate vicinity of the wire.\textsuperscript{129} Prior to \textbf{Publications IV and V}, thermophoretic precipitators, or aerosol deposition tools based on the principle of thermophoresis, have been used widely \textit{e.g.} in aerosol sampling for the study of particle morphologies\textsuperscript{130} and size distributions\textsuperscript{131}, in evaluating the exposure of personnel to airborne nanoparticles\textsuperscript{132-133}, in the deposition of functional coatings of nanoparticles\textsuperscript{134-136} and the deposition of catalyst nanoparticles for surface CVD growth of SWNTs\textsuperscript{137-138}, and using an thermophoretic pellicle to protect lithographic photomasks from particle contamination, created by heating the masks, has been considered.\textsuperscript{139}

Since the size of engineered nanoparticles and nanoparticle agglomerates typically ranges from a few to tens of nanometers, their thermophoretic transport can be described using the
kinetic theory of gases. When a small aerosol particle is suspended in a gas with a temperature gradient, the momentum transfer coming contributed by collisions with “hot” gas molecules will be larger than the momentum transfer from “cold” molecules, resulting in a thermophoretic force acting against the temperature gradient. A graphical depiction of this is presented in Fig. 3.4.1.

Chapman and Enskog suggested that the velocity distribution in an inhomogeneous or non-equilibrium gas can be written as an expansion of perturbations around the Maxwell-Boltzmann velocity distribution presented in Eq. 3.2.10, or

\[ f = f_v + \varepsilon f_1 + \varepsilon^2 f_2 + \cdots \quad (3.4.1) \]

In the case where the inhomogeneity is just a constant temperature gradient in the gas, the expansion can be cut after the first term, which has the form

\[ f_1(v) = f_v \left( 1 - \frac{2}{5} \frac{mk}{n(k_B T)^2} \left( \frac{m v^2}{2k_B T} - \frac{5}{2} \right) v \nabla T \right), \quad (3.4.2) \]

where \( n \) is the number density of the gas, \( \kappa_g = \frac{15k_B m_g}{4m_g} \) is the thermal conductivity of the gas, \( \mu_g \) is the viscosity of the gas, \( m_g \) is the mass of the gas molecule and \( \nabla T \) is the temperature gradient.

![Figure 3.4.1. A graphical depiction of a particle undergoing thermophoresis in free molecular regime. When the particle is suspended in a temperature gradient, the momentum transfer from the hot side of the gradient is larger than the momentum transfer from the cold side, resulting in the thermophoretic force \( F_{th} \) (Eq. 3.2.4). The movement is opposed by the drag force \( F_D \), and in the limit of zero net force on the particle (\( F_{th} + F_D = 0 \)) the particle travels at the thermophoretic terminal velocity.](image)

The thermophoretic force \( F_{th} \) on a small aerosol particle, resulting from collisions with the inhomogeneous gas, can be determined by integrating the momentum transfer coming from
the velocity distribution given by Eq. 3.4.2 over the surface of the particle. Assuming rigid body collisions between the gas molecules and the particle surface, Waldmann determined that the thermophoretic force on a spherical particle is

$$F_{th} = -\frac{4}{15}\sqrt{\frac{2\pi m g}{k_BT}}k_BT\frac{dV}{dP}$$  \hspace{1cm} (3.4.3)

In the limit of disappearing net force on the particle, \(F_D + F_{th} = 0\), where \(F_D\) is given by Eq. 3.2.11 and \(F_{th}\) by Eq. 3.4.3, the particle moves at the thermophoretic terminal velocity

$$v_{th} = -\frac{k_BT}{5(1 + \frac{2\pi m}{k_BT})k_BT} = -\frac{3\mu_gVT}{4(1 + \frac{2\pi m}{k_BT})\rho gT}$$  \hspace{1cm} (3.4.4)

Since Eq. 3.4.4 is independent of the particle size and composition, thermophoretic precipitators designed based on it have been widely used in aerosol science and technology, since in principle non-biased size distributions can be measured from the deposited samples.

In Publication IV, the deposition rate of an SWNT aerosol was experimentally found to be less than predicted by Eq. 3.4.4, and a weak dependence between the deposition rate and nanotube diameter was observed. As the particle size is reduced to the molecular scale, the assumptions of a constant momentum accommodation factor \(\alpha = 0.9\) and rigid body collisions between the gas molecules and the particle surface may no longer be accurate due to intermolecular repulsive forces. Li and Wang have proposed modified forms for the drag and thermophoretic forces accounting for these, resulting in the terminal velocity

$$v_{th} = \left(1 - \frac{6\Omega_{avg}^{(1,2)*}}{5\Omega_{avg}^{(1,3)*}}\right)\frac{k_BT}{Nk_BT} = \left(1 - \frac{6\Omega_{avg}^{(1,2)*}}{5\Omega_{avg}^{(1,3)*}}\right)\frac{15\mu_gVT}{4\rho gT}$$  \hspace{1cm} (3.4.5)

where the reduced collisions integrals \(\Omega_{avg}^{(1,2)*}\) describe the reduced collision probabilities due to intermolecular forces, averaged over diffuse (d) and specular (s) scattering, when considering the drag force \(l = 1\) and the thermophoretic force \(l = 2\). In the treatment of Li and Wang, the intermolecular forces are represented by a so-called 9-3 potential function, originally derived by Rudyak and Krasnolutskii for a gas molecule-nanoparticle surface system where constituent molecules of the gas and the particle interact through the Lennard-Jones potential

$$\Phi(r) = 4\epsilon \left(\frac{r}{a}\right)^{12} - \left(\frac{r}{a}\right)^{6}.$$  \hspace{1cm} (3.4.6)

The reduced collisions integrals in Eq. 3.4.5 can be evaluated using two parametrized equations in Refs. 142 and 143,

$$\Omega_{avg}^{(1,2)*} = \frac{\Omega_{d}^{(1,2)*} + \Omega_{s}^{(1,2)*}}{1 + Kn} - 0.9Kn(\Omega_{d}^{(1,2)*} - \Omega_{s}^{(1,2)*})/\left(1 + \left(\frac{r_p}{2r_p}\right)^{15}\right)$$  \hspace{1cm} (3.4.7)

$$\Omega_{s/d}^{(1,2)*} = 1 + a + \left[aT_0 + \frac{aT_1}{T^{1/4}} + \frac{aT_2}{T^{1/2}}\right]\sigma' + \left[bT_0 + \frac{bT_1}{T^{1/4}} + \frac{bT_2}{T^{1/2}}\right]\sigma'\sigma^2,$$  \hspace{1cm} (3.4.8)

where \(r_p = d_p/2\) is the particle radius, \(Kn = 2d_p/\lambda\) is the Knudsen number, \(a\) and \(b\) are numerical coefficients tabulated in Ref. 143, \(\sigma' = \sigma/r_p\) is the reduced collision diameter, \(T^* =\)
$k_B T / 6\pi \rho_0 \nu_0$ is the reduced temperature, $\nu$ and $\sigma$ are the Lennard-Jones potential parameters, $T$ is the temperature, $\nu = M / \rho_p$ is the effective particle volume per molecule, $M$ is the atomic mass of the particle material, $\rho_p$ is the mass density of the particle, and the coefficients $a$, $b$ have been tabulated in the two publications by Li and Wang. $\nu$ and $\sigma$ can be calculated from the self-interaction Lennard-Jones parameters of the particle and gas materials by the mixing formulae: $\sigma = (\sigma_{\text{particle}} + \sigma_{\text{gas}}) / 2$, $\epsilon = (\epsilon_{\text{particle}} \epsilon_{\text{gas}})^{1/2}$. In practice, Eq. 3.4.7 is a semiempirical model, based on experimental data of momentum accommodation on nanoparticles, which indicates a sharp transition from the value of $\alpha = 0.9$ to purely specular scattering ($\alpha = 0$) as the particle diameter is decreased below 5 nm. Likewise, Eq. 3.4.8 is a parameterized formula based on evaluations of the actual reduced collisions integrals. At particle diameters below 5 nm, the terminal velocities predicted by Eqs. 3.4.4 and 3.4.5 may even differ by orders of magnitude. In the limit of larger particles or temperatures, where the intermolecular forces are less significant, the reduced collisions integrals become $\Omega_x^{(1,1)*} = \Omega_y^{(1,2)*} = 1$, $\Omega_d^{(1,1)*} = 1 + \frac{\pi}{6} - \frac{\pi}{8}$, and the drag force reduces to Eq. 3.2.11, the thermophoretic force to 3.4.3, and the thermophoretic terminal velocity to Eq. 3.4.5.

A thermophoretic force also acts on particles in the transition and continuum regimes, but its magnitude is considerably smaller and it has thus less practical significance as a sampling mechanism. Briefly, the source of the thermophoretic force in the continuum regime is assumed to be a creep velocity directed towards the high-temperature side of the particle, which results in a net force opposite to the temperature gradient. Since in larger particles, a temperature gradient is also established within the particle, the thermophoretic force in the continuum regime is also dependent on the thermal conductivities of the particle and the surrounding gas. In the continuum regime, the thermophoretic force and terminal velocity are according to Brock:

$$ F_{th} = -\frac{9}{2} \pi \frac{\mu_g^2}{\rho_g} d_p \left( \frac{1}{1 + 3C_m K_n} \right) \left( \frac{\kappa_g}{\kappa_p} \frac{\kappa_g + C_t K_n}{1 + 2\kappa_g + 2C_t K_n} \right) \frac{\nabla T}{T} \quad (3.4.9) $$

$$ v_{th} = -\frac{3}{2} \pi \frac{\mu_g^2}{\rho_g} C_c \left( \frac{1}{1 + 3C_m K_n} \right) \left( \frac{\kappa_g}{\kappa_p} \frac{\kappa_g + C_t K_n}{1 + 2\kappa_g + 2C_t K_n} \right) \frac{\nabla T}{T}, \quad (3.4.10) $$

where $\kappa_g$ and $\kappa_p$ are the thermal conductivities of the gas and the particle, respectively, and $C_t$ and $C_m$ are semiempirical coefficients analogous to the momentum accommodation coefficient discussed earlier.

A number of models extending the two cases mentioned above to the transition regime have been published. Initially, Talbot modified the continuum regime equations for the thermophoretic force and terminal velocity by adding interpolating factors that match with the free molecular form of Waldmann at large $Kn$,

$$ F_{th} = -6\pi \frac{\mu_g^2}{\rho_g} d_p C_s \left( \frac{1}{1 + 3C_m K_n} \right) \left( \frac{\kappa_g + C_t K_n}{\kappa_p} \right) \frac{\nabla T}{T}, \quad (3.4.11) $$

$$ v_{th} = -\frac{2\mu_g C_s \left( \frac{\kappa_g}{\kappa_p} + C_t K_n \right)}{\rho_g \left( 1 + 3C_m K_n \right) \left( 1 + \frac{\kappa_g}{\kappa_p} + 2C_t K_n \right)} \frac{\nabla T}{T}, \quad (3.4.12) $$
where \( C_s = 1.17 \), \( C_m = 1.14 \) and \( C_t = 2.18 \) are semi-empirical coefficients, \( \kappa_g \) is the thermal conductivity of the gas, \( \kappa_p \) is the thermal conductivity of the particle, and \( C_c \) is the Cunningham slip correction factor given by Eq. 3.2.9. A review of modified models, including a number of other transition regime models with theoretical basis in the Boltzmann equation, and experiments of thermophoresis, covering both spherical and non-spherical aerosols, has been published by Zheng\(^{147}\). In the free molecular regime, Rosner \textit{et al.}\(^{148}\) have predicted, using an analysis similar to that of Waldmann, that the thermophoretic terminal velocity of spherico-cylinders, or cylinders capped by hemispheres, is close to the velocity of a sphere of the same diameter as the cylinder, when the particle is either randomly or perpendicularly oriented with regards to the temperature gradient. In the case of purely specular collisions, Zurita-Gotor has concluded\(^{149}\) that the thermophoretic velocity should be exactly independent of size and morphology of the particle, as long as the size stays within the free molecular regime and the assumption of specular collisions hold, and equivalent to Eq. 3.3.4 with \( \alpha = 0 \). The arguments of Zurita-Gotor are also expected to hold also when a model conceptually similar to that of Li and Wang\(^{143}\) (Eq. 3.4.5), accounting for non-rigid body collisions, is used. It should be noted that to date, no models for the thermophoresis of non-spherical particles in the transition regime have been proposed, and thus even determining the limits, \textit{e.g.} in terms of particle dimensions and aspect ratios, at which the thermophoretic force and terminal velocity start to deviate significantly from the free molecular regime or continuum regime predictions, is difficult.

### 3.5 Electrostatic transport

Charged aerosol particles in an electric field experience a Coulomb force

\[
F_{el} = i e E, \tag{3.5.1}
\]

where \( i \) is the number of elementary charges on the particle, \( e \) is the elementary charge and \( E \) is the electric field strength. When balanced with the Stokes drag force, the Coulomb force results in a migration velocity of

\[
v_{el} = \frac{i e E}{3 \pi \eta d_p} \tag{3.5.2}
\]

The ratio between the migration velocity and the electric field strength is called the mobility, expressed in aerosol science often by the symbol \( Z \), or

\[
Z = \frac{v_{el}}{E} \tag{3.5.3}
\]

The electrical mobility diameter \( d_{ME} \) of an aerosol particle, measured by the differential mobility analyzers (DMA) described in Chapter 4.3., is the diameter of a singly-charged spherical particle with an equivalent electrical mobility.

In \textbf{Publication I}, bundling in an agglomeration chamber has been observed to lead to an increase in \( d_{ME} \) measured by a DMA, and likewise in \textbf{Publication III}, the postulated bundling-related termination of SWNT growth, and the resulting decreased mean length, has been suggested to correlate with a decrease in \( d_{ME} \). In \textbf{Publication IV}, the number size distribution is used to determine that the FCCVD process is not producing inactive catalyst or other side products that could interfere with the measurement of the thermophoretic terminal velocities.
Similarly to the diffusive equivalent-mobility diameters discussed before, the electrical mobility diameters of non-spherical aerosol particles have been studied in a number of publications, but the particles considered in them, such as MWNTs and metal nanorods, have always had larger diameters and shorter lengths than the SWNTs studied in this work. Kim and Zachariah have suggested, based on measurements of relatively short MWNTs, that the mobility diameter of a non-spherical particle can be related to its physical size simply through the projected area diameter\textsuperscript{159}. In practice, however, longer conductive fibers are expected to orient themselves close to parallel to the electric field lines, which affects the drag force opposing their movement in the electric field and thus the electrical mobility\textsuperscript{125}. The fiber alignment may be further complicated by the combination of a large sheath flow and electric field inside DMAs. Assuming, contrary to the statement above, that an SWNT bundle assumes an orientation parallel to the sheath gas flow, which maximizes its drag force in the direction the applied electric field, Moisala \textit{et al.}\textsuperscript{151} measured the electrical mobility size distributions of short SWNT bundles synthesized using different FCCVD methods and derived a relation for the effective $d_{ME}$ of a bundle based on its physical dimensions, but the bundle populations they studied were shorter by orders of magnitude (with typical bundle lengths of hundreds of nanometers) than the SWNTs studied in \textit{Publications I, III} and \textit{IV}. Nevertheless, a clear difference between the number size distribution measured from an inactive reactor, with no carbon feedstock fed into the process, and an active reactor was observed by them.

The use of electrostatic precipitators (ESP) for depositing thin films of SWNTs grown by the FCCVD method has been reported in a number of earlier publications by Timmermans \textit{et al.}\textsuperscript{152-154} However, the uniformity and morphology of the deposited SWNT thin films deposited using this method are typically not ideal, most likely because of parasitic charging on the dielectric substrates, which leads to local distortion of the electric field\textsuperscript{155-159}.  

4. Methods

4.1 Floating catalyst chemical vapor deposition

In the work contained in this dissertation, three different FCCVD reactors were used for SWNT synthesis. In Publications I and II, the reactor consisted of a 105-cm long quartz work tube inserted into an 87.5 cm long vertical furnace, operated at a set temperature of 880°C. Catalyst particles are produced using a spark discharge generator (SDG) described in detail in Chapter 4.2. In the SDG, a supersaturated iron vapor, which nucleates into Fe nanoparticles, is formed by the physical evaporation of elemental Fe targets caused by high-voltage discharges. The iron particles are carried in a flow of nitrogen (N₂) and mixed with a 250 cm³/min flow of CO (99.5%, AGA), which acts as the carbon feedstock, and a 50 cm³/min flow of hydrogen (H₂, 99.999%, AGA), introduced to ensure the reduction of the catalyst particles to elementary Fe before they enter the reactor furnace. The CO and H₂ flows were controlled by mass flow controllers (Aalborg GFC, Aalborg Instruments & Controls Inc.). The total volumetric flow through the reactor is 500 cm³/min, controlled by a needle valve and critical orifice in a vacuum line and measured using a primary flow calibrator (Gilibrator, Sensidyne, United States).

In Publication I, an agglomeration chamber, consisting of a 120-cm long stainless-steel tube with a circular cross-section and an internal diameter of 6 cm, was used to deliberately agglomerate the SWNT aerosol produced by the reactor. The chamber was connected to the ⅛" stainless steel tubing used at the reactor outlet and the inlets of other instrumentation through two conical expansions. A scanning mobility particle sizer (SMPS+C, consisting of a GRIMM M-DMA differential mobility analyzer and GRIMM 5414 condensation particle counter, GRIMM Aerosol Technik GmbH, Germany) was used to measure the number size concentration of the aerosol at the outlet of the reactor or the agglomeration chamber, and nitrocellulose membrane filters (pore size 0.45 um, diameter 13 mm, Merck Millipore) and the thermophoretic precipitator (TP) described in Chapter 4.4. were used to sample the SWNT aerosol. The sample flow rate through the SMPS+C and TP was 300 cm³/min, and a compensating flow of 200 cm³/min was sampled directly to vacuum using a needle valve and critical orifice in a vacuum line to maintain a total volumetric flow rate of 500 cm³/min through the FCCVD reactor.

In Publication II, the same process was used without the agglomeration chamber. The output of the reactor was mixed with an 800 cm³/min flow of N₂ to obtain a high enough total flow rate for simultaneous deposition of a sample on a nitrocellulose membrane filter (pore size 0.45 um, diameter 47 mm, Merck Millipore) and real-time monitoring of the SWNT number concentration using a condensation particle counter (CPC, TSI 3010, TSI Inc., United States) with a sample flow rate of 1000 cm³/min. The SWNT density on the filter was estimated based on the CPC measurements and divided by the area of the filter, and the deposition was stopped.
automatically when a predetermined density was reached using a solenoid valve. The CPC measurements were recorded and the solenoid valve was controlled by a LabVIEW program.

Figure 4.1.1. a) The FCCVD synthesis scheme used in Publication I. A total flow of 500 cm$^3$/min, consisting of 250 cm$^3$/min of CO, 50 cm$^3$/min of H$_2$, and 250 cm$^3$/min of carrier N$_2$ with catalyst nanoparticles, passes through the FCCVD reactor. The scheme is similar to the process described earlier in Mustonen et al., except that an agglomeration chamber with an estimated residence time of 5 min at a flow of 500 cm$^3$/min is used to promote the agglomeration of the SWNT aerosol. When using the thermophoretic precipitator (TP), a sample flow of 300 cm$^3$/min is passed through the TP and the remaining 200 cm$^3$/min pass through a bypass line. Similarly, when using the SMPS+C system, 300 cm$^3$/min are sampled by the SMPS+C internal pump and the remaining 200 cm$^3$/min are sampled from the process using the vacuum line, controlled by a needle valve.

b) The FCCVD synthesis scheme used in Publication II. In a manner similar to a), a total flow of 500 cm$^3$/min passes through the FCCVD reactor. The flow is mixed with an additional 800 cm$^3$/min of nitrogen at the outlet of the reactor to create a total flow of 1300 cm$^3$/min, out of which 1000 cm$^3$/min is sampled by the CPC and 300 cm$^3$/min through a 47-mm nitrocellulose filter. The sampling time is controlled using a computer-controlled solenoid valve, which closes when a predetermined density on the filter, determined by the CPC measurements, is reached.

In Publications III and IV, the reactor consisted of an 85-cm quartz work tube (internal diameter 25.8 mm) inserted into a 55.5 cm long vertical furnace, operated at set temperatures of 825°C (Publication III) and 850°C (Publication IV). The slight change in the operation temperature was based on re-optimization of the temperature profile during reactor maintenance. In this process, Fe catalyst nanoparticles are produced by the thermal decomposition of ferrocene (dicyclopentadienyl iron, C$_2$H$_{10}$Fe, 99%, Alfa Aesar, Germany) in the top part of the CVD furnace. A suitable temperature profile is created by inserting a water-cooled injector structure 8.5 cm into the furnace. Three flows of CO (99.5%, AGA) were introduced into the furnace: a ca. 200-250 cm$^3$/min flow directly through the water-cooled injector, a ca. 50-100 cm$^3$/min flow first through a water-cooled ferrocene saturator cartridge and then through the water-cooled injector, and a 100 cm$^3$/min flow to the space between the water-cooled injector and the inner wall of the quartz work tube, to prevent flow recirculation near the top of the furnace. The sum of the two flows introduced through the injector was kept at 300 cm$^3$/min; the specific values of the flows depended on the desired synthesis condition. All CO flows were controlled by mass flow controllers (Aalborg GFC, Aalborg Instruments & Controls Inc., United States). Additionally, a small flow of CO$_2$ was introduced into the process to modulate the length, and in Publication IV, the diameter of the grown SWNTs. In Publication III, the CO$_2$ flow was controlled using a MFC similar to those used to control the CO flows, and in Publication IV, the CO$_2$ flow was controlled using a mass flow controller designed for low volumetric flow rates (Sierra MicroTrak 101, Sierra Instruments, Inc., United States) for better control.
over the CO₂ concentration. In all publications, SWNTs were collected either by using the thermophoretic precipitators (TP) described in Ch. 4.4 or on nitrocellulose membrane filters (pore size 0.45 μm, diameters 13 mm, 23 mm and 47 mm; Merck Millipore) attached to the outlet of the reactor. The sample flows were controlled by a needle valve and critical orifice in a vacuum line and measured using a primary flow calibrator.

![Figure 4.1.2. a) The FCCVD synthesis scheme used in Publication III. b) The FCCVD synthesis scheme used in Publications IV-V. In Publication V, a scaled-up version of a similar process was used to synthesize SWNTs for wafer-scale thermophoretic deposition of thin films. In the scaled-up process, the height of the furnace was 87 cm and the length of the quartz work tube was 105 cm. The upper temperature zone of the furnace was heated to 850°C and the lower temperature zone to 730°C.]

4.2 Aerosol generation by spark discharge

In Publications I-II, a spark discharge generator (SDG) was used to generate iron nanoparticles for catalyzing the SWNT growth and in Publication IV, for the generation of iron nano-agglomerates for comparing the thermophoretic deposition rate of SWNTs against an aerosol expected to follow Waldmann’s free molecular regime model for thermophoresis (Eqs. 3.4.3 - 3.4.4). The spark discharge method for generating aerosol nanoparticles was originally introduced by Schwyn et al., and is used in the production of metal and carbon nanoparticles for a range of academic and industrial applications.

The specific SDG design used here has been described in detail in Mustonen et al. The generator is built inside a cross-shaped 5-way KF25 vacuum fitting. The spark discharge occurs between two rod-shaped electrodes of elemental iron (diameter 6 mm, 99.95%, Goodfellow, United Kingdom), which are fitted inside insulating PTFE cylinders inserted into two opposing ports so that the separation of the electrode faces is ca. 1 mm. The fifth port (not pictured in Fig. 4.2.1) is used for visual inspection of the discharge through a quartz viewport. Discharge between the electrodes is achieved by charging a high-voltage capacitor (C = 55 pF for catalyst production, C = 2 nF for producing the nano-agglomerates in Publication IV), connecting the electrodes, through a series resistor (R = 1.5 MΩ) using a high voltage source (Matsushita HV Amplifier, Matsushita, Japan in Publications I-II, Heinzinger PNC 20000, Heinzinger GmbH, Germany in Publication IV) until a discharge occurs, and the discharge rate (typically...
on the order of 1 kHz), determining the quantity of evaporated material, can adjusted by the applied charging voltage. The discharge is flushed by a jet of N₂ created by passing a high volumetric flow through a nozzle. Each discharge is expected to generate an approximately constant number of primary particles, so the number concentration of primary particles generated is

\[ N_p = n_0 \frac{f}{Q}, \]  
(4.2.1)

where \( f \) is the discharge frequency and \( Q \) is the volumetric flow rate of gas through the discharge. For the production of the nano-agglomerates studied in Publication IV, a smaller volumetric flow rate, adjusted based on the mobility size distribution measured by an SMPS+E instrument described in Chapter 4.3, was used.

![Figure 4.2.1. A cut-out schematic of the SDG used in Publications I, II and IV. The discharge occurs between the two rod-shaped horizontal iron electrodes and is flushed using a nitrogen jet passing through the nozzle. The resulting primary aerosol exits through the top of the SDG and is passed either to a FCCVD reactor or to an SMPS+E for measurement of the particle size distribution.](image)

### 4.3 Aerosol measurements

The measurement of aerosol size distributions is widely used in the monitoring of air quality due to the hazards aerosols may pose to human health, and in the development of combustion engines and other machinery causing these emissions. In this work, aerosol measurement tools have been used to measure the electrical mobility size distributions of nanoparticles and aerosol-synthesized SWNTs in Publications I, II and IV, and to determine the concentration of SWNTs produced by the aerosol synthesis process, which in turn has been used to deposit SWNT coatings with a predefined surface density in Publications III and IV and evaluate the efficiency of the thermophoretic precipitators studied in Publications IV and V.

A scanning mobility particle sizer (SMPS) measures electrical mobility size distributions of aerosols by classifying particles by their electrical mobility, given by Eq. 3.3.3, with a differential mobility analyzer (DMA) and counting the number concentration of particles with each mobility. When the particle counting is carried out using a condensation particle counter (CPC), the abbreviation SMPS+C is used for specificity; likewise, when the counting is carried out using a Faraday cup electrometer (FCE), the abbreviation SMPS+E is used. The operating principles of the component instruments are explained below. The mobility size distribution measured by an SMPS is typically plotted in a log-linear scale, to account for the usually log-
normal size distributions of aerosols. In practice, the aerosol is classified in discrete-size bins, or channels, of mobility diameters. A common convention in aerosol science is to plot the vertical axis in units of $\frac{dN}{d\log_{10}d_{ME}}$, indicating that the bin count $dN$ has been normalized with the logarithm of the channel width, or

$$\frac{dN}{d\log_{10}d_{ME}} = \frac{dN}{\log_{10}d_{ME,u} - \log_{10}d_{ME,l}} \quad (4.3.1)$$

where $d_{ME,u}$ and $d_{ME,l}$ are the upper and lower bounds of the channel, expressed in electrical mobility diameters. The rationale behind this convention is that the plots of distributions measured with different numbers of diameter channels appear visually similar to each other, and the normalized concentrations $\frac{dN}{d\log_{10}d_{ME}}$ at the mode of the distribution are approximately the same.

The differential mobility analyzer (DMA) classifies aerosol particles according to their electrical mobility, defined in Eq. 3.5.3. The DMAs used in this dissertation use a so-called Vienna-type geometry published by Winklmayr et al.\textsuperscript{160} and Reischl et al.\textsuperscript{161}, where the aerosol and carrier gas move in a cylindrical column between a grounded cylindrical shell and a cylindrical center electrode. The column is flushed with a laminar sheath air flow of particle-free air in order to create a velocity profile suitable for particle classification. The sample aerosol flow enters the DMA at the outside edge of the column, and the particles move toward the walls at a velocity determined by their electrical mobility. At the opposite end of the DMA column, particles of a given mobility diameter $d_{ME}$, determined by the DMA geometry, the flows, and the electric field strength between the electrodes, exit through a slit, while all other particles are either carried out from the DMA with the sheath flow or deposited on the electrodes. In practice, the size range which can be classified by a DMA is limited by the dielectric strength of air, which limits the electric field which can be applied. Larger particles, which could be potentially harmful for the DMA, are normally removed from the sample aerosol flow using an inertial impactor at the aerosol inlet. In practice, the aerosol classified by a DMA is not completely monodisperse with regards to $d_{ME}$ due to multiple charging of the aerosol, diffusive transport, and possibly nonidealities in the flow inside the DMA, and the actual output from a DMA set to a particular electrical mobility or mobility diameter is in practice a narrow distribution of mobilities, peaking at the set value.

To make classification by the electrical mobility diameter meaningful in terms of the particle dimensions, the aerosol must be brought to a known steady state charge distribution. This is typically done by exposing the carrier gas to ionizing radiation, typically produced using a solid radiation source or a soft X-ray source, and diffusive collisions with ions bring the aerosol to an equilibrium charge distribution. In the presence of bipolar ions, the equilibrium charge distribution can be determined based on Fuchs\textsuperscript{162}, or in the submicron range relevant in this work, using a numerically less involved approximation by Wiedensohler\textsuperscript{163}. At the moment of writing, experimental data on the bipolar charging efficiency of non-spherical and particularly high aspect ratio aerosol particles is limited, but typically indicates that the charging efficiency of non-spherical particles is higher than that of spherical particles of equivalent electrical mobility diameters\textsuperscript{164-166}. Tandem DMA measurements of FCCVD SWNTs, carried out using two consecutive DMAs, indicate that they may carry up to five elementary charges\textsuperscript{167}.
Two models of DMAs were used in the publications contained in this dissertation. In Publications I, II, III and IV, a GRIMM M-DMA (GRIMM Aerosol Technik GmbH & Co. KG, Germany) was used as part of a scanning mobility particle sizer. In the M-DMA, the length of the DMA column is 88 mm and the inner diameter of the ground electrode and the outer diameter of the high voltage electrode are 40 mm and 26 mm, respectively. The sheath air flow and the sample aerosol flow are 3 l/min and 0.3 l/min. The electrical mobility size range that the M-DMA can classify is, based on manufacturer specification, 5.4 – 358 nm. In Publication IV, and in tuning the catalyst particle size and concentration for the FCCVD process used in Publications I and II, a Grimm nano-DMA (GRIMM Aerosol Technik GmbH & Co. KG, Germany) was used, also as part of a scanning mobility particle sizer. In the nano-DMA, the length of the DMA column is 15 mm and the inner diameter of the ground electrode and the outer diameter of the high voltage electrode are 40 mm and 26 mm, respectively. The sheath air flow and the sample aerosol flow used in the measurements are 20 l/min and 1 l/min, respectively. The electrical mobility size range that the instrument can classify at a sample flow of 1 l/min is, based on manufacturer specification, 0.9 – 112 nm.

Direct optical counting of particles with $d_p < 50$ nm is not practically possible. The condensation particle counter (CPC, sometimes also referred to as a condensation nucleus counter, or CNC) is used to grow optically measureable droplets of a working fluid, typically 10-12 μm in diameter, around aerosol particles using the principle of heterogeneous condensation. The number concentration of droplets can in turn be measured optically using a diode laser and photodetector either by direct counting, if the droplet number concentration is low enough, or photometrically (by measuring the total loss of intensity) in the case of higher concentrations. When aerosol particles, or condensation nuclei, move through a supersaturated vapor, droplets can grow around them even at relatively low supersaturations by heterogeneous nucleation. The supersaturation, or the ratio between the actual vapor mixing ratio and the saturation vapor mixing ratio, is typically expressed in percents. At a sufficiently high supersaturation, referred to as the critical supersaturation, droplets will also form spontaneously by homogeneous nucleation, since clusters of vapor molecules start to act as condensation nuclei. The critical supersaturation for homogeneous nucleation is typically around 300%, while droplets may form by heterogeneous nucleation already at supersaturations of less than 1%. In CPCs, the supersaturation, determined by the saturator and condenser temperatures, is typically set
to a high value below the critical supersaturation, so that homogeneous nucleation of droplets does not happen in particle free gas. The minimum particle size, typically expressed as the diameter at which 50% of the particles can be detected by a CPC, is determined by the Kelvin equation. For heterogeneous nucleation to occur, the supersaturation ratio $p_d/p_s$ needs to exceed the value

$$\frac{p_d}{p_s} = \exp \left( \frac{4V_m \gamma}{RT d_p} \right), \quad (4.3.2)$$

where $V_m$ is the molar volume of the CPC working fluid, $\gamma$ is the surface tension, $R$ is the ideal gas constant and $d_p$ is the particle diameter. In CPCs using the diffusional thermal cooling method, such as the instruments used in this work, the aerosol carrier gas is saturated by passing it through a channel surrounded by a heated porous wick, wetted with the working fluid, and condensation happens in a cooled condenser.

![Schematic illustration of a differential mobility analyzer](image)

**Figure 4.3.2** a) Schematic illustration of a differential mobility analyzer. The inset photographs show the aerosol and sheath flow inlet part of the Grimm M-DMA and the central electrode, with the inlet part and the outer electrode removed. The sample aerosol enters the column through the small radial openings. The sheath flow enters through the white membrane seen on the bottom of the inlet part. The exit slit is marked by an orange arrow on the photograph of the center electrode. b) Schematic illustration of a condensation particle counter.

Two models of CPCs, both using 1-butanol as the working fluid, were used in the publications contained in this dissertation. In **Publications I, III, IV and V** a GRIMM model 5414 CPC (GRIMM Aerosol Technik GmbH & Co. KG, Germany) was used both independently and as part of an SMPS+C system. The manufacturer specifications of the instrument are a particle size cutoff $d_{50}$ of 4 nm, and counting accuracies of 5% for single-particle counting (for number concentrations below $1.5 \times 10^5$ cm$^{-3}$), and 10% for photometric counting (for number concentrations between $1.5 \times 10^5$ and $10^7$ cm$^{-3}$) In **Publication II**, a TSI 3010 CPC (TSI Inc., United States) was used to provide real-time information about the SWNT number concentration. The manufacturer specifications of the instrument are a particle size cutoff of 10 nm, and a counting accuracy of $<10\%$ for single-particle counting (for number concentrations below $1 \times 10^4$ cm$^{-3}$).
Charged aerosol particles may be also counted using a Faraday cup electrometer (FCE), similar in principle to the FCEs used to determine electron beam doses. The aerosol FCE consists of a high loading capacity filter held in a so-called Faraday cup, which is electrically well insulated from its surroundings. As charged aerosol particles deposit on the filter, the Faraday cup gains a net charge, which is discharged through a high-resistance feedback resistor, and the net current contributed by the aerosol particles can be measured using an electrometer placed across the resistor. In Publication IV, and in tuning the catalyst particle size and concentration for the FCCVD process used in Publications I and II, a Grimm model 5705 FCE (GRIMM Aerosol Technik GmbH & Co. KG, Germany) was used as part of a scanning mobility particle sizer.

4.4 Thermophoretic precipitators

Two plate-to-plate thermophoretic precipitators (TP), both designed and built for the purpose of this work, were used to deposit SWNTs for their characterization and for the fabrication of TFTs and TCFs in Publications I, III, IV, and V. The smaller of these, designed for the deposition of SWNTs or other nanoscale aerosols on centimeter-scale chips, is described in detail in Publication IV. The TP consists of two aluminum plates separated by a PTFE plate, in which a rectangular flow channel has been cut. The substrate is located on the lower plate in a rectangular, 0.5 mm deep recession and is surrounded by a smaller 0.5 mm thick PTFE plate with a hole in the shape and size of the substrate so that when depositing 0.5 mm thick Si/SiO$_2$ chips, the top surfaces of the substrate and the smaller PTFE plate form the bottom of the flow channel. The top plate is heated using two aluminum housed power resistors (approximate maximum heating power 84 W), and the bottom plate is cooled by ambient temperature water cooling. The temperatures of the TP plates were monitored using K-type thermocouples (Fluke Corp., United States) clamped to the plates. Because of the low thermal conductivity of the PTFE plate separating the hot and cold plates, at full heating power, a temperature gradient on the order of 10$^5$ K m$^{-1}$, estimated as the temperature difference of the hot and cold plates divided by the height of the upper PTFE plate, could be attained over the 0.25 or 0.5 mm high channel. The aerosol enters and exits the channel through the upper plate through two 1/4 in. pipes. A schematic of the TP components and the flow channel defined by the inlets and PTFE plates is presented in Figure 4.4.1.

![Figure 4.4.1. Schematic representation of the plate-to-plate TP used in Publications I, III and IV and the flow channel defined by the plates and b) the cut in the upper polytetrafluoroethylene (PTFE) plate (inset). Copyright American Chemical Society, used with permission.](image-url)
A scaled-up precipitator, used for deposition of SWNT TCFs on 50-mm wafers and PET sheets, is described in detail in Publication V. A cut-out graphic and a side profile of the TP design are shown in Figure 4.4.2a and 4.4.2b. The aerosol enters the TP through a 25-mm vacuum flange connected to an expansion in the shape of a truncated cone (height 100 mm, top diameter 65 mm, bottom diameter 95 mm) and passes through a 60 mm long and 0.4 mm wide rectangular orifice on a hot plate, heated using thin-film resistors (Omega Engineering Ltd., United Kingdom) with a total heating power of 56 W. The target substrate is placed on a water-cooled stage, with lateral dimensions of 100 × 90 mm, which can be moved along the lateral axis perpendicular to the orifice, and vertically, to adjust the distance and temperature gradient between the substrate and the hot plate, using two stepper motors controlled by a positioning controller (PI GmbH & Co KG, Germany). To increase the uniformity of the deposited coating, the sample chuck can be oscillated under the orifice as shown in Figure 4.4.2c. The movement speed of the oscillation is 1.25 mm/s. The carrier gas exits through two ¼” outlets parallel to the ends of the orifice, placed symmetrically 20 mm below the top of the lower chamber of the TP. In all experiments in Publication V, the hot plate was heated to a temperature of 90°C and the sample chuck was held at an ambient temperature of ca. 23°C using water cooling. The separation between the substrate and the hot plate was kept at 0.75 mm, corresponding to a temperature gradient of approximately 9.3 × 10⁴ K/m, and a volumetric flow of 300 cm³/min through the TP, controlled using a needle valve and critical orifice in a vacuum line, was used.

Figure 4.4.2. a) A schematic illustration of the scaled-up depositor design used in Publication V. b) A profile view of the deposition area, viewed towards the end of the heated plate orifice. c) The oscillation procedure for depositing uniform thin films.

4.5 Microfabrication

The common back gate TFTs in Publications II-IV were fabricated using common microfabrication techniques. Starting from thermally oxidized wafers (100 nm of SiO₂) of highly doped silicon, the oxide layer on the device side of the wafer was covered in spin-coated photoresist (AZ5214E, Microchemicals GmbH, Germany), after which the oxide layer on the uncovered side of the wafer was wet etched in buffered hydrofluoric acid. As the gate contact, 250 nm of aluminum was sputtered on the etched side. The protective photoresist was then removed using acetone in an ultrasonicator bath. The TFT test arrays were prepared on ca. 1.5 cm x 1.5 cm
chips cut from the wafer. First, source and drain contacts were defined by photolithography and electron beam evaporation of 5 nm of titanium and 40 nm of gold, followed by lift-off in acetone. Then, SWNTs were deposited on the source and drain contacts either from a nitrocellulose filter (Publications II–III), which was attached on the chip using a droplet of isopropyl alcohol and dissolved by soaking the filter and chip in room-temperature acetone overnight, or using a thermophoretic precipitator (Publication IV). The SWNT channels were defined by photolithography, after which SWNTs located outside the intended channels were removed using reactive ion etching by an O$_2$/Ar plasma. The protective photoresist on the channels was lift-off using a commercial photoresist remover (AZ100, Microchemicals GmbH, Germany), after which the chips were washed in isopropyl alcohol and dried using filtered nitrogen.

![Figure 4.5.1.](image)

**Figure 4.5.1.** a) Schematic of the microfabrication procedures on the device side of the chip. Prior to the first step, SiO$_2$ has been etched from the backside of the chip and a 250-nm layer of Al has been sputtered as a gate contact. b) Photograph of a finished TFT test array similar to those fabricated in Publications II–IV. The finished array contains 634 TFTs of different channel dimensions.

In Publication III, SWNTs were collected on micropatterned filters fabricated based on an earlier protocol published by Fukaya et al.\textsuperscript{169} and provided by the authors of that publication. Briefly, polyvinylidenedifluoride (PVDF) membrane filters with a pore size of 0.45 μm were treated with a CF$_4$ plasma to enhance their hydrophobicity, after which a 1 μm thick layer of photoresist (Shipley S1813G, Dow Electronic Materials) was spin coated on them and patterned using standard photolithography techniques. The fabricated rectangular gratings had approximately 8 μm wide traces with 50, 100, 200 and 400 μm spacings, connected by perpendicular lines spaced at 2000 μm.

### 4.6 Electrical and optical characterization

Conducting thin films of metals and doped semiconductors are commonly characterized by their sheet resistance $R_s$, which is the resistivity $\rho$ scaled by the conducting layer thickness $t$, because $t$ is often difficult to determine. The resistance $R$ of a rectangular slab of material, with length and width $L$ and $W$ and thickness $t$ relates to the sheet resistance $R_s$ through

$$R = \frac{\rho L}{t W} = \frac{\rho L}{t W} = \frac{R_s L}{W}.$$  \hspace{1cm} (4.6.1)

The sheet resistances of SWNT thin films in Publications I, III, and V were characterized using a linear four-point probe (Jandel Engineering Ltd., United Kingdom), consisting of spring loaded tungsten tips (radius of curvature 100 μm, needle load 60 grams, spacing between tips 1.0 mm) arranged in a row, combined with a four-terminal multimeter (HP 3458, Hewlett Packard).
In the four-point probe, separate pairs of current-carrying, or force, and voltage-sensing, or sense, electrodes are used, which eliminates the lead and contact resistances from the measurement thus allowing the accurate measurement of small values of resistances. A schematic of the probe geometry is shown in Figure 4.6.1. The two outer force probes carry current $I$, and the voltage $V$ is measured between the two inner sense probes. In the case of a linear four-point probe with equal spacing $s$ measuring an infinite, thin ($t/s < 0.4$) sheet, the sheet resistance and the current-voltage response are related by

$$R_s = \frac{\pi}{\log 2} \frac{V}{I},$$  \hspace{1cm} (4.6.2)

where the factor of $\pi/\log 2$ is specific to the measurement geometry. Eq. 4.6.2 is valid also for finite sheets under the conditions that the probe spacing is small compared to the lateral dimensions of the sample and that the probes are located far from the edges, and similar factors have been derived also for other probe geometries.

![Figure 4.6.1. Geometry of the four-point probe. A current $I$ is supplied through the two outer force probes, and the generated voltage drop $V$ is measured between the inner sense probes. The sheet resistance of the sample can be determined by Eq. 4.6.2 when the sample thickness $t$ is small compared to the probe distance $s$ and the sample is large compared to the probe dimensions.](image)

In Publications III and V, the SWNT TCFs were hole doped using nitric acid (HNO$_3$, ACS reagent grade, 70%, Sigma Aldrich) by drop casting HNO$_3$ on the SWNT films, waiting for 60 seconds and washing the films using deionized water. The films deposited on PET in Publication V were doped using a 16-mM solution of gold (III) chloride ($\geq$99.99% trace metals basis, Sigma Aldrich) in acetonitrile (electronic grade, 99.999% trace metals basis, Sigma-Aldrich). The solution was drop cast on the SWNT films, left in place for 5 minutes, and washed off using acetonitrile. The mechanism of hole doping TCFs is discussed in detail in Chapter 2.5.

The optical absorption spectra in Publications I-IV were measured using a double-beam Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. In all measurements, low-hydroxyl quartz glass slides (Heraeus HSQ300, Heraeus Quarzglas GmbH & Co. KG, Germany) were used as the substrates. In Publication V, optical absorption spectra were measured using a double-beam Agilent Cary 5000 UV-Vis-NIR spectrophotometer, and 5-cm borosilicate glass wafers (Microchemicals GmbH, Germany) or 100 μm thick PET sheets were used as the substrates for thermophoretically deposited films. Quartz glass slides similar to those used before and smaller PET sheets were used as the substrates for the press-transferred samples. In all measurements, a clean substrate was used with the reference beam of the spectrophotometer to exclude absorption on the substrate. The positions of the $S_{11}$ and $S_{22}$ signatures, and an
empirical atlas of transitions\textsuperscript{27} and modified tight binding model calculations\textsuperscript{26}, were used to determine the mean diameter of the SWNTs.

The TFT transfer characteristics in \textbf{Publications II-IV} were measured using an Agilent 4156B semiconductor parameter analyzer connected to a semi-automatic probe station (PA200, Karl Suss AG, Germany) capable of executing programmed stage movements. The TFTs characterized in \textbf{Publications II-IV} were non-passivated and thus exhibited significant hysteresis, and p-type behavior caused by ambient molecules. The characterization used is based on the standard models of p-type FETs, and the device mobility was inferred from linear-regime measurements. In the linear regime of operation, when the source-drain bias $V_{DS}$ is small compared to the difference of the gate voltage $V_{GS}$ and the threshold voltage $V_{th}$ and $V_{GS} > V_{th}$, the source-drain current $I_D$ is linearly dependent on $V_{DS}$, and can be approximated as

$$I_D = \frac{W_{CH}}{L_{CH}} C \mu (V_{GS} - V_{th})V_{DS},$$

(4.6.3)

where $C$ is the gate-channel capacitance per unit area, and $\mu$ is the field-effect mobility. The field-effect mobility may be extracted from transfer curve measurements. The response between the gate bias and the source-drain current is called the transconductance, which is, based on Eq. 4.6.3,

$$g_m = \frac{dI_D}{dV_{GS}} = \frac{W_{CH}}{L_{CH}} C \mu V_{DS},$$

(4.6.4)

and the field-effect mobility $\mu$ can be extracted from the measurements and device dimensions using

$$\mu = \frac{L_{CH}}{W_{CH} V_{DS} C} \frac{1}{\frac{dI_D}{dV_{GS}}},$$

(4.6.5)

Per usual practice in the literature\textsuperscript{100}, $\mu$ was reported based on the maximum of the transconductance and as discussed before, Eq. 2.5.2. was used to determine $C$, with SWNT dimensions and densities determined by optical absorption spectroscopy and scanning electron microscopy was used to maintain comparability with earlier published results and to avoid underestimation of the field-effect mobility caused by use of the parallel plate model.

4.7 Raman spectroscopy

In \textbf{Publication III}, Raman spectra were obtained using a Horiba Jobin-Yvon Labram HR Raman spectrometer (Horiba, Japan). Three beamline,s with an argon laser operating at 514 nm, a helium-neon laser operating at 633 nm, and an infrared diode laser operating at 785 nm were used. The spectrometer uses a thermoelectrically cooled CCD detector and an Olympus BX-41 microscope equipped with 10×, 20×, 50×, and 100× magnification objectives, and a 1800 mm\(^{-1}\) grating with a spectral resolution of 1 cm\(^{-1}\).
4.8 Scanning electron microscopy and image analysis

Scanning electron microscopy (SEM) was used to determine the surface densities and length distributions of SWNTs in all publications contained in this dissertation. In the SEM, an electron beam is produced by an electron gun and focused and accelerated using a set of magnetic and electrostatic lenses. The most common imaging mode in SEM is based on the detection of secondary electrons, which are produced when primary electrons eject free, low-energy electrons from the sample atoms through inelastic scattering. The number of produced secondary electrons depends, among other things, on the materials, topography and charging state of the sample surface. Topographic imaging is usually carried out using a so-called Everhart-Thornley detector, which collects secondary electrons using a positively biased grid, located in the sample chamber above the sample. The diameter of an SWNT is in principle too small to be imaged using the conventional secondary electron contrast mechanism of the SEM. However, when a SWNT on a thin insulating surface, such as the oxide layer on a Si/SiO₂ chip, is observed at a low acceleration voltage (ca. 1 kV) by an in-column-type secondary electron detector, which can detect low-energy electrons, the insulator surface around the SWNT is imaged in high contrast, providing bright images of individual SWNTs. A number of mechanisms has been suggested for this: Brintlinger et al. have proposed that the contrast arises from the surface potential difference between the SWNT and the substrate and Homma et al. have proposed that the contrast is caused by electron-beam-induced conductivity and an induced current in the insulator surface.

![Figure 4.8.1](image_url)

Figure 4.8.1. a) A schematic depiction of a scanning electron microscope similar to the Zeiss Sigma VP SEM used in this work. Partially adapted from Ref. 173 under the Creative Commons Share-Alike 3.0 license. b) A schematic depiction of secondary electron production through inelastic scattering. c) A representative micrograph of iron oxide nanoparticle agglomerates similar to those studied in Publication IV. d) A representative micrograph of SWNTs on a Si/SiO₂ substrate, imaged using an in-column SE detector at an acceleration voltage of 1 kV.

In the publications contained in this dissertation, a Zeiss Sigma VP SEM (Carl Zeiss GmbH), using a Schottky-type FEG, was used for all imaging. With the exception of the iron nano-agglomerates produced in Publication IV, which were imaged using a conventional secondary electron detector, all samples were studied using the in-column secondary electron detector and an acceleration voltage of ca. 1.0 kV, adjusted slightly when needed. Typically, the sample substrates were Si/SiO₂ chips with a 100 nm thick thermally grown oxide layer.
In Publications I-III, the SEM micrographs were analyzed using the Adobe Photoshop CC (Adobe Systems Inc., United States) image editing software. SWNT densities were recorded by hand using a counting tool and SWNT and bundle lengths by manually drawing a freeform selection around the SWNTs and dividing the perimeter length of the selection by 2. In Publication IV, measurement of the SWNT length and orientation distributions was carried out using FiberApp\textsuperscript{174}, a free MATLAB-based tool for measuring fibrous objects from different types of micrographs. The tool allows the user to select a small number of points along the fiber, which is tracked using a variety of pathfinding algorithms and contour models described in detail in Usov and Mezzenga\textsuperscript{174}. In Publication V, gtFiber, a similar free MATLAB-based tool for automatic detection of orientational order from micrographs of fibrous objects, was used to determine the orientation distributions of SWNTs from SEM micrographs. gtFiber uses a number of filtering and thresholding steps to thin the fibers in the micrographs to single-pixel skeletons, from which the orientation distribution can be measured. A detailed description of the tool has been published by Persson et al.\textsuperscript{175} The filter and threshold settings used in Publication V were determined empirically by visual inspection of the original and filtered micrographs.

The length distributions of aerosol-synthesized SWNTs normally follow a log-normal distribution of the form

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp \left( -\frac{(\ln(x-\mu))^2}{2\sigma^2} \right), \quad (4.8.1)$$

where $\mu$ and $\sigma$ are the distribution parameters. Length distributions were fitted to measured data using the maximum likelihood estimators

$$\hat{\mu} = \frac{\sum_k \ln x_k}{n}, \quad \hat{\sigma}^2 = \frac{\sum_k (\ln x_k - \hat{\mu})^2}{n}, \quad (4.8.2)$$

where $x_k$ are the observations and $n$ is the total number of observations. In Publications IV and V, the magnitude of orientation in the imaged SWNTs was quantified using the two-dimensional order parameter $S_{2D}$, defined by

$$S_{2D} = 2(\cos^2 \theta_n) - 1, \quad (4.8.3)$$

where $\theta_n$ is the angle between an individual fiber pixel and the average orientation of the entire image.
4.9 Atomic force microscopy

Atomic force microscopy (AFM) was used in Publications I-V to study the degree of bundling of thermophoretically deposited SWNTs and the morphology of SWNT thin films utilized as TFT channels and TCFs. All imaging was carried out in the intermittent contact, or tapping, imaging mode. In the tapping mode, the AFM cantilever is oscillated at a frequency matching or nearly matching its resonance frequency (on the order of tens or hundreds of kHz for the cantilevers used) using a piezoelectric actuator. The distance between the cantilever tip and the sample is determined by the drive amplitude. When the tip closes in on the sample surface, intermolecular and electrostatic forces exerted on it typically damps (but may in certain cases increase) the oscillation amplitude of the cantilever to some value lower than the free drive amplitude. This is compensated by lifting the cantilever away from the sample until a set oscillation amplitude, typically close to the drive amplitude with cantilever-tip interactions need to be minimized, is reached. When the tip is scanned over the sample surface, the necessary compensation varies from point to point, and it is recorded to produce an image of the surface topography.

All imaging in the publications was carried out using a Veeco Dimension 5000 AFM (Veeco Instruments Inc., United States). In Publications I and III, pieces of cleaved muscovite mica (V-4 grade, Electron Microscopy Sciences, United States) were used as the substrate, on which SWNTs were thermophoretically deposited. In Publications II and IV, the TFT channels were imaged in their finished state after microfabrication and in the Publication V, the TCFs were imaged immediately after thermophoretic deposition or press transfer.

Due to the forces exerted on the sample in tapping mode, soft and elastic structures may be compressed by the tip, which in turn leads to an underestimation of their height. The manipulation of SWNTs using an AFM operating in tapping mode was first reported by Postma et al.\textsuperscript{176}, who also reported a dependence between the observed SWNT diameter and the drive amplitude used in imaging. This property has been used to measure the radial elasticity of SWNTs with different diameters using a well-calibrated AFM\textsuperscript{177,178}. Certain newer models of AFMs are also capable of constant-force imaging, where the peak interaction force applied by the tip can be controlled quantitatively, and a dependence between the observed network height in SWNT thin films and the applied force, controlled in this manner, has been reported\textsuperscript{179}. In Publications I and III, the drive amplitude and amplitude set point were adjusted carefully so that the observed mean height of structures identified as non-bundled
SWNTs approximately matched the mean diameter measured using optical absorption spectroscopy, but a slight, less than 20%, measurement error is still possible, particularly in the case of the SWNTs measured in Publication III.

![Diagram](image.png)

**Figure 4.9.1.** a) A schematic depiction of the AFM parts. b) A schematic depiction of the AFM height signal formation in tapping mode imaging. c) A representative an AFM micrograph similar to those studied in Publications I and III, and a profile measurement (corresponding to the line marked with 1 on the micrograph).

### 4.10 Numerical methods

In Publication II, the contribution of purely geometric variations, i.e. the fact that even with well-determined average densities, the TFT channels are different random networks with the same average SWNT density, to the spread of the $I_{ON}/I_{OFF}$ ratio was studied using an equivalent circuit model. In the model, line segments, with a length distribution matching the measured length distribution of the SWNTs, are randomly and isotropically placed in a rectangular cell corresponding to the channel dimensions and an equivalent circuit is formed by considering each line segment to be a circuit node and placing a resistor between all intersecting segments. Two opposing sides of the cell are treated as the source and drain terminal. The resistance between the source and drain terminal is solved using Modified Nodal Analysis (MNA). In the specific case where the circuit under consideration contains $n$ nodes, $m$ independent voltage sources, and no current sources, MNA amounts to solving the linear system

$$AX = Z$$  \hspace{1cm} (4.10.1)

where the unknown $(n+m \times 1)$ vector $X$ contains the node voltages in its upper $n$ entries and the currents at each voltage source contained in the system in its lower $m$ entries, the $(n+m \times 1)$ vector $Z$ contains zeroes in its upper $n$ entries and the voltages of each voltage source contained in the system in its lower $m$ entries, and $A$ is a block matrix defined by the matrices $G$ and $B$,
\[ A = \begin{bmatrix} G & B \\ B^T & 0 \end{bmatrix} \]  

(4.10.2)

\( G \) is a \( m \times m \) conductance matrix, with the off-diagonal elements \( G(i,j) \) containing the negative of the conductance \( G_{ij} \) between the \( i \)th and \( j \)th circuit nodes (zero if \( i \) and \( j \) are not connected) and the diagonal elements \( G(i,i) \) containing the sum of conductances between the node \( i \) and other nodes. \( B \) is a \( m \times n \) voltage source matrix, describing the locations of \( n \) voltage sources so that \( B(m,n) = 1 \), if the positive terminal of the \( n \)th voltage source is connected to node \( m \), \( B(m,n) = -1 \), if the negative terminal of the \( n \)th voltage source is connected to node \( m \), and \( B(m,n) = 0 \) otherwise. In the simulations carried out in Publication II, each line segment was assigned an electronic type, with \( 2/3 \) of the segments being semiconducting and \( 1/3 \) metallic, and the contact resistances determining \( G \) were picked according to Table 4.10.1. The junction resistances were selected based on published values using two- and three-terminal measurements of crossed SWNTs by Fuhrer et al.\(^71\) and conducting AFM measurements of SWNT junctions by Znidarsic et al.\(^93\), although particularly the junction resistance between metallic and semiconducting SWNTs had to be scaled to much higher values than reported in either publication to account for the low experimentally observed \( I_{\text{OFF}} \). Physically, the high assumed contact resistance could result from a wide depletion zone formed in the semiconducting SWNT near the Schottky barrier formed at the junction.

**Figure 4.10.1.** An illustration of the equivalent circuit model used in Publication IV. The equivalent circuit is built by placing line segments with a length distribution matching the measured SWNT length distribution in a rectangular cell, registering intersections with the segments or the two edges of the cell representing the source and drain terminals, and building an equivalent circuit where the line segments are represented by nodes and the intersections between them by resistors.

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<td>Gated (OFF state)</td>
<td>500 kΩ</td>
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**Table 4.10.1.** Values of contact resistances between different types of SWNTs in the equivalent circuit model in Publication II. The values were partially based on Fuhrer et al.\(^71\) and Znidarsic et al.\(^93\); significantly higher values than were experimentally observed in these studies were used for the OFF state resistances of semiconducting-to-metal and semiconducting-to-semiconducting SWNT junctions, to account for the high OFF state resistances observed in Publication II.

In Publication V, combined heat transfer and computational fluid dynamics (CFD) simulations of the scaled-up TP were carried out using COMSOL Multiphysics 5.3, a commercial partial differential equation solver that uses the finite element method with adaptive meshing and a variety of numerical solvers. A picture of the geometry and mesh used in the simulations...
is shown in Figure 4.10.2. The mesh was manually refined in the region inside the TP hot plate and above the sample. As boundary conditions, the inner surfaces of the hot plate were set to 363 K, the inlet gas temperature and cold plate surfaces were set to 296 K, the inlet pressure was set to 1 atmosphere and the outlet flow rate was set to correspond to an outflow of 150 cm$^3$/min, to account for two symmetric outlets. The part of the TP near the flow expansion and the deposition zone was modelled and split in half to decrease the size of the geometry, and symmetric boundary conditions were applied on the cross-sectional surfaces seen in Figure 4.10.2 for both heat transfer and CFD. Flow in the rest of the lower chamber of the depositor was assumed to be insignificant, since the outlets are located in the vicinity of the sample stage. The computations were carried out using the Nonisothermal Flow module in COMSOL, combining CFD using the Laminar Flow module and heat transfer using the Heat Transfer in Fluids module.

**Figure 4.10.2.** The geometry and finite element mesh used in the heat transfer and computational fluid dynamics simulations in *Publication V*. Inset: A close-up of the mesh near the hot plate orifice.
5. Results and summary

5.1 Diffusive agglomeration of SWNTs

In Publication I, the gas-phase bundling of SWNTs due to diffusive transport and its effect on the performance of TCFs fabricated using SWNT aerosols with different bundle sizes were studied using an agglomeration chamber connected to the FCCVD process. As mentioned in Chapter 2.5, a number of prior publications have postulated that an increase in the degree of bundling, or the mean bundle size, has a negative effect on the performance of SWNT TCFs. These studies have shared the experimental shortcomings that the bundle size and length could not be controlled separately, or that different bundle sizes were obtained e.g. by using different ultrasonication times and powers, which can also have an effect on the defectivity of the SWNT.

A summary of the agglomeration-related results of Publication I is presented in Figure 5.1.1. Three SWNT populations labelled i), ii) and iii), corresponding to different synthesis conditions, were used in the studies. In condition i), the FCCVD process was run at a relatively low concentration (with a measured number concentration of $2.35 \times 10^5$ cm$^{-3}$ at the outlet of the reactor), in condition ii), at a higher concentration (with a measured number concentration of $1.12 \times 10^6$ cm$^{-3}$ at the outlet of the reactor) and in condition iii), at a higher concentration similar to condition ii), and the SWNT aerosol was passed through a separate agglomeration chamber connected to the FCCVD reactor. Increasing the concentration of the synthesis process was observed to increase the mean electrical mobility diameter measured using a SMPS+C, and measuring the distribution through the agglomeration chamber resulted in a ca. 70% decrease in the number concentration, from $1.12 \times 10^6$ cm$^{-3}$ to $3.24 \times 10^5$ cm$^{-3}$. The bundle length distributions from conditions i) and ii), measured from SEM micrographs of bundles deposited on Si/SiO$_2$ chips using the small-scale TP presented in Chapter 4.4., were practically identical, with mean lengths of 3.0 and 3.1 $\mu$m, respectively, whereas the increased bundling in condition iii) lead to an increased mean length of 3.8 $\mu$m. Likewise, the bundle diameter distribution, measured from AFM micrographs of bundles deposited using the TP on exfoliated mica substrates, showed that increasing the number concentration increased the mean diameter from 1.38 nm to 1.80 nm, corresponding to averages of approximately 1.6 and 2.7 SWNTs per bundle, based on Eq. 2.3.3 and a mean SWNT diameter of 1.1 nm. Passing the SWNTs through the agglomeration chamber further increased the mean bundle diameter to 2.90 nm, corresponding to approximately 7 SWNTs per bundle. Eqs. 2.3.3 and 3.3.13 can be combined to predict the increase in mean bundle diameter due to agglomeration by

$$d_b(t) \approx d_{CNT} \sqrt{\frac{<n_0>}{K_\phi N_0 t}}, \quad (5.1.1)$$

where $d_b$ is the bundle diameter, $d_{CNT}$ is the mean diameter of the constituent SWNTs, $<n_0>$ is the initial mean number of SWNTs in the bundles, $K_\phi$ is the slip-corrected monodisperse
agglomeration coefficient given by Eq. 3.3.11, where the Cunningham slip correction factor has been evaluated at the mobility diameters used below, $N_0$ is the initial number concentration, and $t$ is the time.

Based on numerical solutions of Eqs. 3.3.12 and 5.1.1., the observed decrease in the number concentration and increase in the bundle diameter could be predicted to a high accuracy when mobility diameters $d_M$ in the range of 10-30 nm were used to determine the slip-corrected agglomeration coefficient by Eq. 3.3.11. The numerical predictions for $N$ and $d_b$ in a situation corresponding to condition iii), starting from the number concentration and bundle diameter of condition ii) and assuming a mobility diameter of $d_M = 20$ nm and transport through the agglomeration chamber at a volumetric flow rate of 500 cm$^3$/min, were $N = 4.04 \times 10^5$/cm$^3$ and $d_b = 2.91$ nm. The value of $d_b$ matches the bundle diameter observed by AFM well, but $N$ is overestimated by ca. 20%. Using $d_M = 10$ nm, the corresponding predictions were $N = 3.4 \times 10^5$/cm$^3$, $d_b = 3.6$ nm, indicating that $N$ matched the observed value accurately, but $d_b$ was overestimated even when accounting for the experimental error in properly done AFM measurements. A possible source for the slight discrepancy observed are diffusive losses to the agglomeration chamber walls and tubing, but they were estimated to be small based on Eq.
ca. 2.2% assuming \(d_M = 20\) nm, \(L = 120\) cm and \(Q = 500\) cm³/min, and were not accounted for.

It should be noted that using the measured \(d_M\) to estimate e.g. diffusive deposition may be misleading, since the collision rate and diffusive transport are in practice determined by different effective diameters, the mobility diameter \(d_M\) and an effective collision diameter \(d_C\), signifying the mean distance, at which two non-spherical particles collide and stick together. The monodisperse agglomeration coefficient defined in Eq. 3.3.11 can in principle be rewritten as

\[
K_\phi = \frac{8k_BTd_C}{3\mu_gd_M^2C_c} \quad (5.1.2)
\]

where \(d_C\) is the effective collision diameter. \(d_C\) can be expected to depend on the non-spherical particle dimensions and its rotational diffusivity, and an analytical treatment in the case of fractal agglomerates has been published by Zurita-Gotor and Rosner\(^{181}\). In the case of a high aspect ratio structure such as an SWNT, it can be assumed that \(d_C > d_M\), and evaluating \(d_M\) solely based on the monodisperse agglomeration rate likely underestimates it.

If the value of \(d_M = 20\) nm is nevertheless used as an equivalent mobility diameter, it corresponds to a slip-corrected diffusion coefficient of \(1.4 \times 10^{-8}\) m²/s at room temperature based on Eqs. 3.2.8 and 3.2.9, which is significantly higher than predicted by several published models of the diffusion coefficients of non-spherical particles. For example, Buckley et al.\(^{127}\) have predicted that the mobility diameter of a fiber-like particle with a diameter of 2 nm and a length of 3 μm is approximately 70-80 nm, depending on the orientation relative to the surrounding gas flow, and corresponding to diffusion coefficients between \(1-1.3 \times 10^{-9}\) m²/s. In Mädler and Friedlander\(^{126}\), it is demonstrated that simply assuming that the drag force, normalized by velocity, of a chain-like agglomerate is the sum of the normalized drag forces of its constituent particles gives qualitatively good prediction compared to several more complex models of agglomerate mobility and a widely used model for cylindrical particles by Dahneke\(^{182}\). If population ii) in Figure 5.1.1. is treated as a chain consisting of \(d_p = 1.8\) nm primary particles, the slip-corrected diffusion coefficient of the primary particle is ca. \(1.6 \times 10^{-6}\) m²/s and that of a 3100-nm long chain is \(9.5 \times 10^{-10}\) m²/s, close to the prediction of Buckley et al.

To summarize, while using \(d_M = 20\) nm in the monodisperse approximation predicts the agglomeration rate with a good accuracy, it likely overestimates e.g. losses caused by diffusive transport. It is, however, not certain that existing models for the diffusive mobility of fibers and other non-spherical particles are valid for extremely thin fibers such as SWNTs, and e.g. ultrathin asbestos fibers have been observed to have higher diffusion constants than predicted by theoretical models of chain-like agglomerates and cylindrical particles, based on measurements using diffusion batteries\(^{125}\). Similarly, the mobility diameters of FCCVD SWNTs could be measured in a follow-up experiment, using a setup similar to that of Publication IV, with the thermophoretic precipitator replaced by a diffusion battery. Since most published models predict that the drag force acting on a fiber-like particle is proportional to the length, this technique could possibly also be used to remove shorter SWNTs due to their higher diffusivities, thus providing one route to gas-phase length-based fractionation of SWNTs.

### 5.2 The effect of bundling on SWNT TCF properties

In Publication I, a semi-empirical model of TCF performance, relating the figure of merit \(K\) defined in Eq. 2.5.3 to the bundle size and SWNT length, was derived based on a study of the
three SWNT populations. The model is built on three assumptions. First, it is assumed that the absorbance is a linear function of the amount of SWNTs in the film, and possible differences in the absorptivity of different types of SWNTs are averaged over given the large numbers of SWNTs present in a TCF. Second, it is assumed that electrical conduction in a non-doped and non-biased film happens only through junctions between metallic SWNTs, since junctions between semiconducting SWNTs or SWNTs of mixed types have contact resistances that are orders of magnitude higher\(^7\). Third, it is assumed that the electrical conductivity along a bundle is not significantly better than the conductivity along individual SWNTs, while junctions between bundles are more conductive than junctions between individual SWNTs. These assumptions immediately lead to the conclusion that most SWNTs in large bundles are “dead mass” from the viewpoint of electrical conduction and contribute only to optical absorption, and thus reducing the degree of bundling improves the TCF performance.

Assuming a fixed mean length of 3 μm, the value of \(K\) as a function of the bundle was determined to be, based on characterization of TCFs from the three different conditions studied in Publication I,  

\[
K(n) = K_0 \beta \left(\frac{\langle l_{CNT}\rangle}{6}\right) \left(1 - \left(\frac{2}{3}\right)^n\right) \quad (5.2.1),
\]

where \(K_0 = 34.2 \pm 3.5 \text{ k}Ω^{-1}\) is an ideal quality factor, obtainable in the limit of completely individual SWNTs, in the case of the \(\langle l_{CNT}\rangle = 3 \text{ μm}\) SWNTs studied in Publication I, \(\beta = 2.67\) is a fitting parameter accounting for improved contacts between bundles (a value of \(\beta = 1\) would correspond to no improvement), \(n\) is the number of SWNTs in a bundle, and the final term accounts for the fact that when 1/3 of the SWNTs are metallic, the probability for a bundle to contain a metallic pathway, contributing to the electrical conductivity in a non-biased and non-doped network, is approximately \(1-(2/3)^n\). The SWNT films used as TCFs are typically thicker than a monolayer, and for densities far above the percolation threshold, the conductance, given the same amount of material in the network, is expected to increase roughly linearly with the mean SWNT or bundle length \(\langle l_{CNT}\rangle\).\(^46\) Eq. 5.2.1 can be extended to account for this, giving

\[
K(n, l_{CNT}) = \Pi \left(\frac{\langle 1-(2/3)^n\rangle l_{CNT}}{\langle n\rangle}\right), \quad (5.2.2)
\]

where \(\Pi = \frac{\beta K_0}{l_{CNT,\alpha}} = 30.4 \pm 5.8 \text{ μm}^3\text{k}Ω^{-1}\) is a reference value based on the performance measured in Publication I, from which Eq. 5.2.2. extrapolates the performance of TCFs consisting of other SWNT lengths and bundle sizes. Eq. 5.2.2 was also used to retrospectively evaluate the TCF performances obtained in Mustonen et al.\(^{120}\) and Kaskela et al.\(^{46}\) and was found to match well, although the bundle diameters and the lengths of their constituent SWNTs were not reported in the original publications and had to be estimated retrospectively based on the reported bundle lengths. Eq. 5.2.2 can be also used to evaluate the maximum achievable performance of uniform SWNT-based TCFs. A fourth, implicit assumption behind the model is that the TCF resistance is dominated by junctions between SWNTs. However, the Ohmic resistance along SWNTs or bundles reaches the junction resistance between metallic SWNTs at a distance between 10 – 20 μm, meaning that increasing \(\langle l_{CNT}\rangle\) should no longer improve the performance. A conservative estimate, based on the assumption that this happens at \(\langle l_{CNT}\rangle = 10 \text{ μm}\), gives a maximum \(K\) of approximately 114 kΩ^{-1} for films consisting of individual SWNTs of
mixed electronic types, corresponding to a sheet resistance of 80 Ω/sq. at 90% transmittance. Correspondingly, a purely metallic or doped network could reach a value of 25 Ω/sq. at 90% transmittance, and no uniform SWNT-based TCF published to date has reached this value.

In **Publication III**, the effects of bundling were studied in a FCCVD process with ferrocene as the catalyst precursor and CO as the carbon feedstock, and the number concentration of the process was tuned by changing the mixing ratio of pure CO and CO carrying ferrocene vapor, fed into the process. Three synthesis conditions with number concentrations of $2 \times 10^6$ cm$^{-3}$ (referred to as “high concentration”), $1.2 \times 10^6$ cm$^{-3}$ (“medium concentration”) and $0.25 \times 10^6$ cm$^{-3}$ (“low concentration”) were studied. As in **Publication I**, TCFs were collected on filters and press transferred on quartz substrates for characterization, and the small-scale TP was used to deposit samples for the measurement of bundle height distributions using AFM and bundle length distributions using SEM. The TCF performance was found to depend strongly on the number concentration. TCFs collected from the low concentration exhibited a sheet resistance of 89 Ω/sq. at 90% transmittance after doping by HNO$_3$, and TCFs from the medium and high condition exhibited sheet resistances of ca. 120 and 440 Ω/sq. at 90% transmittance, respectively.

The mean bundle height was observed to be 1.20 nm for SWNTs synthesized using the low concentration, 1.61 nm for SWNTs synthesized using the medium concentration and 2.36 nm for SWNTs synthesized using the high concentration. Considering that the mean diameter of the SWNTs was 1.3 nm based on UV/Vis/NIR spectroscopy, the AFM measurements likely underestimated the height by ca. 30%, since the measured heights of structures assumed to be individual SWNTs were close to 1 nm.
Figure 5.2.2. a) Sheet resistances and optical transmittance of SWNT TCFs collected from different process conditions in Publication III, a) before doping and b) after doping with HNO3. Reducing the number concentration of the process resulted in a systematic improvement in TCF performance, with the non-doped sheet resistances at a transmittance of 90% decreasing from 5, to 1.3 and 0.95 kΩ/sq. as the concentration is decreased from high (2 × 10^6 cm⁻³) to medium (1.2 × 10^6 cm⁻³) and low (0.25 × 10^6 cm⁻³). The trend was maintained in TCFs treated with HNO3, resulting in sheet resistances of 440, 120 and 89 Ω/sq. at 90% transmittance, respectively. 

c), d) and e) Bundle height distributions measured by AFM and bundle length distributions measured by SEM for the low, medium and high concentration conditions, respectively. Copyright Elsevier, used with permission.

SWNTs from the low concentration condition were also used to fabricate TCFs with a microgrid pattern, based on a protocol published earlier by Fukaya et al. For the microgrid TCFs, SWNTs were collected using a filter, on which a rectangular microgrid pattern consisting of 8 μm wide lines with different spacings, connected by perpendicular lines spaced at 2000 μm intervals, had been previously defined by photolithography. While the transmittance of the SWNT lines collected at the grid openings can be very low, the limited resolution of the human eye (typically reported to be 300-400 dots per inch, or details larger than 75 μm) makes the grid appear uniform at normal viewing distances. A photograph of microgrid SWNT TCFs on a flexible poly(ethylene naphthalate) (PEN) substrate, and an optical micrograph and SEM micrographs of the finished SWNT microgrid structure are shown in Figure 5.2.3a, c, d and e. In correspondence with the results reported by Fukaya et al., the microgrid patterned TCFs displayed lower sheet resistances at equivalent optical transmittances, suggesting that similar patterning techniques may be one route to surpass the projected limits of SWNT TCF performance stated earlier.

It should be noted that the non-doped and uniform SWNT TCFs in Publication III (Fig. 5.2.2a) underperform the films measured in Publication I, and thus the model built on their TCF performance, or Eqs. 5.2.1 and 5.2.2. One possible reason for this can be a difference handling of the films: In Publication III, the films showed a strong, over 10-fold improvement in sheet resistance when treated with HNO3, indicating that their so-called pristine values were likely not affected by doping by atmospheric molecules, which can decrease the sheet resistance by a factor of 2 in a short period of time after the SWNT film has been exposed to them. If the values measured from HNO3 doped films in Publication III are interpreted using Eqs. 5.2.1 and 5.2.2, by assuming that the doped films correspond to an all-metallic network, the obtained values of 440, 120 and 89 Ω/sq. at <l_CNT> = 4.8, 4.2, and 2.9 μm would correspond to <n> = 1.37, 1.6, 4.1, or <d_b> = 1.5 nm, 1.77 nm, 2.91 nm. When accounting for experimental error in the AFM measurements, estimated to be ca. 30% above, these values match reasonably well with the bundle heights observed by AFM. The discrepancy between Publications I and
III suggests that careful attention should be paid to the conditions, at which non-doped SWNT TCFs are stored and measured.

![Image](image_url)

**Figure 5.2.3.** a) Photograph of microgrid patterned SWNT TCFs on a PEN substrate, with four different grid spacings corresponding to different transmittances. The patterned TCFs appear visually uniform at typical viewing distances of 30 to 60 cm. b) Comparison of micro-patterned and uniform SWNT TCFs along with reference data, showing that the highly individual SWNT films collected from the low concentration condition are competitive with other SWNT-based TCFs reported earlier. The reference data is reproduced from Nasibulin et al. [111], Kaskela et al. [46], Wu et al. [94], Kaempgen et al. [183], Geng et al. [184], and Fukaya et al. [169]. c) Optical micrograph of a grid line pattern with a 50 \( \mu \)m spacing. d) and e) SEM micrographs showing the micro-structure of a patterned SWNT TCF. The thin diagonal lines visible in c) and d) are caused by hairline cracks in the photoresist layer, which in turn is caused by shear stress induced by the filter holder mechanism. Copyright Elsevier, used with permission.

### 5.3 Density controlled SWNT films by aerosol monitoring

In Publication II, a real-time measurement of the number concentration in a FCCVD synthesis process was used to collect SWNT thin films with predetermined densities on filter membranes. Likewise, in Publication IV, predicted densities of SWNT thin films based on CPC measurements and the precipitator geometry were compared against measured densities from SEM micrographs, to demonstrate that thin films with predetermined densities based on CPC monitoring can be deposited also using the TP. The predicted surface density \( \rho \) of an SWNT thin film is assumed to follow

\[
\rho = \frac{nCQt}{A} \quad (5.3.1)
\]

where \( \eta \) is the efficiency of the deposition method, assumed to be unity for the filter and calculated using a procedure explained in detail in Chapter 5.4 in the case of the small scale TP, \( C \) is the measured number concentration of the SWNT aerosol (real-time in Publication II, average of pre-deposition and post-deposition measurements in Publication IV), \( t \) is the collection time and \( A \) is the area of the filter or the depositor channel. In Publication II,
SWNT films with predetermined densities near the percolation thresholds given by Eq. 2.5.1 and shown in Figure 2.5.2 were collected on filters by measuring the number concentration of the synthesis process in real time from a diluted side flow, and stopping the filtration when a predetermined density was reached. The densities measured from SEM micrographs of the SWNT films, transferred on Si/SiO₂ chips by filter dissolution, were found to be in a good agreement with the prediction of Eq. 5.3.1. A plot of the predicted surface density versus the measured surface density and representative SEM micrographs are presented in Figure 5.3.1.

![Figure 5.3.1](image)

**Figure 5.3.1.** a) Comparison of set and measured surface densities of five different samples, with increasing target densities in the range 0.36 μm⁻² to 1.8 μm⁻². A good correspondence is observed, verifying the validity of the CPC-based real-time concentration monitoring and controlled deposition system used in Publication II. b) Representative SEM micrographs of the samples measured for a). Copyright American Chemical Society, used with permission.

A set of TFT arrays was fabricated using the collected films as channels, to test how accurately the line segment percolation model discussed in Chapter 2.5 predicts the behavior of TFTs fabricated from SWNTs with mixed electronic types, and to demonstrate the high TFT yield achievable with the controlled deposition system. The percolation threshold for an infinite system is given by Eq. 2.5.1., and based on the numerical simulations depicted in Figure 2.5.2, the practical threshold for achieving 100% percolating channels are approximately 25% higher. With a mean length of 4 μm, the percolation thresholds for mixed, purely semiconducting and purely metallic channels are 0.352 μm⁻², 0.529 μm⁻² and 1.057 μm⁻², respectively, or if scaled up by 25%, 0.44 μm⁻², 0.66 μm⁻² and 1.321 μm⁻². These values corresponded well with the behavior shown in Figure 5.3.2. A significant number of devices with a set SWNT density of 0.36 μm⁻² had no percolating path and thus had a low I.ON, or were not conductive at any V.GS, practically all devices with a set SWNT density of 0.72 μm⁻² operated as intended and had a high I.0NS/I.OFF ratio, and I.0NS/I.OFF started to degrade due to metallic pathways when the set density was increased to 1.08 μm⁻² and above. Transfer curves of 40 TFTs for each SWNT density, with L.CH = W.CH = 100 μm, and V.DS = -1 V are shown in Figure 5.3.2.

![Figure 5.3.2](image)

**Figure 5.3.2.** Transfer curves for SWNT TFTs with different set SWNT densities (40 devices per density) covering the range from sub-percolating thin films (< 0.4 μm⁻²) to the metallic SWNT percolation threshold (> 1.0 μm⁻²). L.CH = W.CH = 100 μm and V.DS = -1 V in all devices. Copyright American Chemical Society, used with permission.

At the optimal set density of 0.72 μm⁻², 643 out of 644 tested TFTs in the test array, consisting of 100 μm, 200 μm and 500 μm wide devices with channel lengths of 5, 10, 20, 30, 40, 50 and 100 μm (40 W.CH = 100 μm devices, 32 W.CH = 200 μm devices and 20 W.CH = 500 μm devices...
for each channel length, for a total of 644 devices) were observed to operate as expected, and high $I_{ON}/I_{OFF}$ ratios were achieved when the channel length exceeded 20 μm. The transfer curves of all characterized $W_{CH} = 100$ μm devices are shown in Figure 5.3.3a. The spread in $I_{ON}/I_{OFF}$ was compared against the equivalent-circuit model described in Chapter 4.10, which in principle represents an ideally dispersed network with uniform junction properties. The equivalent-circuit model predicted the experimentally observed spread in $I_{ON}/I_{OFF}$ within each set of device dimensions well, and also reproduced the experimentally observed sudden decrease in $I_{ON}/I_{OFF}$ when $L_{CH} < 20$ μm. A comparison of experimentally observed and simulated values of $I_{ON}/I_{OFF}$ is shown in Figure 5.3.3b. The fact that the spread is predicted by the relatively simple model indicated that the SWNTs were well dispersed and the density was high enough that variations in e.g. junction conductivities are effectively averaged over. The slope of the relation between $I_{ON}$ and $L_{CH}$ was observed to change at approximately $L_{CH} = 20$ μm, indicating that at this channel length, the finite length of the channel causes the probability of a purely metallic pathway to increase significantly, which increases $I_{ON}$ and degrades $I_{ON}/I_{OFF}$. This indicates that at least for SWNTs with mixed electronic types, miniaturization of the devices is limited by the fact that $L_{CH}$ should be approximately five times larger than the mean SWNT or bundle length.

Since the comparison of devices fabricated using different set densities indicated that the density of unsorted SWNT TFT channels cannot be increased without a significant loss in $I_{ON}/I_{OFF}$, the results of Publication II may be close to the highest performance and yield achievable using small-diameter (d = ca. 1.1 nm) unsorted FCCVD SWNTs and the transfer method based on filter dissolution. Conversely, the ability to fabricate TFTs with higher SWNT densities than the limits set by Eq. 2.5.1 and confirmed experimentally in Publication II, while simultaneously having high $I_{ON}/I_{OFF}$ ratios, may be taken as indication that a synthesis process grows preferentially semiconducting SWNTs or that some post-processing treatment removes metallic SWNTs selectively.
Figure 5.3.3. a) Transfer characteristics of 280 W_{CH} = 100 \, \mu m \, TFTs with different channel lengths, fabricated from a SWNT thin film with the optimal surface density of 0.72 m^{-2}. b) I_{ON}/I_{OFF} ratios as a function of channel length for channel widths of 100, 200, and 500 \, \mu m, respectively, showing the increase of median (solid circles) I_{ON}/I_{OFF} current ratio as a function of increasing channel length. The distribution of experimentally realized I_{ON}/I_{OFF} ratios approaches the spread of numerically simulated ideal networks (N = 250 for each channel length) above L_{CH} = 40 \, \mu m. c) I_{ON} measured at V_{DS} = -1 \, V, V_{GS} = -10 \, V, normalized by channel width for all 644 TFTs, as a function of the channel length. Copyright American Chemical Society, used with permission.

5.4 Thermophoretic transport of SWNTs

In Publication IV, the thermophoretic terminal velocities of SWNTs with different diameters, and for comparison, iron nano-agglomerates with a mean electrical mobility diameter d_{ME} of ca. 50 nm, were studied by measuring the decrease in the number concentration, when the aerosol was passed through the small-scale TP presented in Figure 4.4.1 during a heating and cooling cycle. The deposition efficiency of the TP as a function of the temperature gradient \nabla T, estimated to be the temperature difference between the hot and cold plate divided by the channel height, was estimated to be the ratio between the number concentration C(\nabla T) measured at a temperature gradient \nabla T, and the number concentration measured when both sides of the TP were at ambient temperature, C(\nabla T = 0), or

\[ \eta_{exp}(\nabla T) = \frac{C(\nabla T)}{C(\nabla T = 0)}. \]  (5.4.1)

A representative example of simultaneous measurements of the number concentration and temperature gradient during a heating and cooling cycle is shown in Figure 5.4.1. The TP was heated to the maximum hot plate temperature and cooled down to room temperature, and the number concentration measured after the TP was observed to be inversely proportional to the temperature gradient.

The measurement can be also presented in terms of the experimental deposition efficiency \eta_{exp} defined in Eq. 5.4.1, resulting in a linear relationship between \nabla T and \eta_{exp}. Assuming that the aerosol spreads evenly in the vertical direction of the rectangular TP flow channel after entering it, the deposition efficiency is approximately
where $V_{th}$ is the mean thermophoretic velocity in the channel, calculated using Eq. 3.4.4 using the mean of the hot and cold plate temperatures as the particle temperature $T$, $t_{res,x} = l/Qwh$ is the lateral residence time in the channel, where $l$ is the length of the channel, $Q$ is the volumetric flow rate through the TP, $w$ is the width of the channel and $h$ is the height of the channel.

In practice, Eq. 5.4.2 amounts to the assumption that particles moving at $V_{th}$ will deposit if their vertical displacement given by $v_{th}$ and $t_{res,x}$ is equal or more than the channel height $h$. The effective length of the channel was assumed to be 50 mm, or the distance between the inlet and outlet tubes shown in Figure 4.4.1b, and a channel width of 20 mm, defined by the cut in the upper flow guide plate, was used in all measurements. Representative measurements of $\eta_{exp}$ versus $VT$ (out of a set of six measurements per material) and $\eta_{th}$ versus the measured $VT$ are shown in Figure 5.4.2a. In the case of the iron nano-agglomerates, $\eta_{th}$ and $\eta_{exp}$ matched closely, indicating that they deposit at the velocity predicted by Eq. 3.4.4, while the experimental deposition efficiencies $\eta_{exp}$ of the SWNT aerosols were observed to be lower. The terminal velocities of the SWNTs, expressed relative to the prediction of Eq. 3.4.4., were evaluated by carrying out six measurements with two different channel heights and three different volumetric flow rates, and comparing the slopes of a linear fit of $\eta_{exp}$ versus $VT$ against a linear fit of $\eta_{th}$ versus $VT$. The average thermophoretic terminal velocities of SWNTs with mean diameters of 1.2 nm, 1.5 nm and 1.9 were observed to be 35%, 39% and 43% of Eq. 3.4.4., respectively. The experimentally observed rates were also compared to predictions calculated using the model of Li and Wang, or Eq. 3.4.5, using the mean SWNT diameters (determined by UV/Vis/NIR spectroscopy) as the particle diameters, the Lennard-Jones parameters $\sigma_{CO} = 0.3652$ nm, $\epsilon_{CO} = 0.8181$ kJ/mol, $\sigma_{CNT} = 0.34$ nm, $\epsilon_{CNT} = 0.3612$ kJ/mol, the mass of a carbon atom $M_C = 2\times10^{-26}$ kg, and the theoretical SWNT mass density $\rho_{CNT} = 2000$ kgm$^{-3}$. $\epsilon$ and $\sigma$ were calculated from the material parameters using the mixing formulae $\sigma = (\sigma_{CNT} + \sigma_{CO})/2$, $\epsilon = (\epsilon_{CNT}\epsilon_{CO})^{1/2}$. A comparison between a prediction based on Li and Wang and the experimentally observed terminal velocities is shown in Figure 5.4.2b. While the observed trend of a terminal velocity decreasing with the SWNT diameter qualitatively matches the model of Li and Wang, the magnitudes of the velocities were smaller than predicted by the model. A similar observation has been published by Zhang et al., who measured the deposition rates of flame synthesized titanium oxide nanoparticles in the size range of $d = 7.5$ nm – 14 nm, and reported that the experimentally observed terminal velocity of 7.5 nm particles was approximately 60% of the prediction of Eq. 3.4.4, while the model of Li and Wang predicts a value of approximately 85%. Another theoretical study by Wang et al., considering the case of sphero-cylindrical
particles using a framework similar to Li and Wang, was published simultaneously with Publication IV, but the predictions it makes (a thermophoretic terminal velocity of approximately 75% of Eq. 3.4.4, for SWNTs with \( d = 1 \) nm in argon at 300 K) are close to those of Li and Wang or larger. Together with the observations by Zhang et al.\textsuperscript{188}, the findings in Publication IV indicate that the mechanisms of thermophoresis of nanoscale particles and SWNTs are likely not completely described by the theoretical models published to date.

Figure 5.4.2. a) Experimentally observed (blue circles) and theoretical (red solid line) deposition efficiencies for iron nano-agglomerates and SWNTs with different diameters in a 0.5 mm high and 20 mm wide TP channel at volume flows close to 300 cm\(^3\)/min. b) Comparison of the experimentally observed thermophoretic terminal velocities and the model of Li and Wang, using the SWNT mean diameters as the particle diameters. Copyright American Chemical Society, used with permission.

Following Zurita-Gotor\textsuperscript{149}, it can be argued that the length and bundle size distributions measured from thermophoretically sampled SWNTs should be nonbiased, as long as the SWNT diameter distribution stays relatively narrow and the slightly different deposition rates for different diameters will not result in significant bias. This is normally the case with FCCVD processes similar to those used in this dissertation, and the relatively weak diameter dependence in the diameter range accessible with the FCCVD method means that even if the diameter and length are strongly correlated, SWNTs with different lengths should be sampled with nearly similar efficiencies. Examples of length distributions measured from SEM micrographs of thermophoretically deposited SWNTs are shown in Figure 5.4.3., and with a large sample size, the shape of the length distribution is observed to be log-normal, as expected. So far, it seems that the length distributions of even significantly longer or shorter SWNTs grown by a FCCVD process, such as an ethanol-based process recently published by Ding et al.\textsuperscript{190}, can be accurately measured from thermophoretically deposited samples. In Publication IV, all of the studied SWNTs were synthesized using approximately the same process concentrations, and thus the degree of bundling should stay relatively constant across the different populations. In the case of agglomerates of spherical particles, Zurita-Gotor has also argued that all agglomerates of spherical particles with locally concave shapes should have the same thermophoretic terminal velocities as their constituent particles. Considering the closely packed geometry of SWNT bundles, the same argument should apply also to them, and this could be confirmed by a follow-up study of Publication IV using a larger range of concentrations. In Publication IV, the possibility that the high aspect ratios and thermal conductivities of SWNTs could disturb the temperature gradient locally, and thus result in a diminished thermophoretic terminal velocity similar to that predicted for spherical particles in the transition
regime, is also briefly discussed. However, since the SWNTs can be assumed to be aligned perpendicular to the temperature gradient in the geometries used in Publications IV and V, lengthwise thermal conduction should not result in such a disturbance. Such an effect could be also assumed to result in a length dependence of the thermophoretic deposition rate, which was not evident in the length distributions of sampled SWNTs measured in Publications IV and V.

Figure 5.4.3. a) Representative SEM micrographs of deposited Fe agglomerates (scale bar 1 μm) and SWNTs (scale bars 2 μm). b) Length distributions measured from deposited SWNTs. The solid red curves are log-normal maximum likelihood fits (μ = 8.16, σ = 0.58 for d = 1.2 nm SWNTs; μ = 7.82, σ = 0.43 for d = 1.5 nm SWNTs; and μ = 7.78, σ = 0.71 for d = 1.9 nm SWNTs) on the measured data. Copyright American Chemical Society, used with permission.

In principle, the thermophoretic force and thermophoretic terminal velocity could also be measured directly using a Millikan cell or electrodynamic balance, in which the thermophoretic force is balanced against an electrostatic force by applying a potential between the hot and cold plates. Examples of such measurements are included in the review by Zheng 147. These techniques are in principle applicable also to SWNTs, but their use is complicated by the charging of the SWNT aerosol, which may carry multiple elementary charges, and as discussed earlier, may behave differently from commonly used models when being neutralized by bipolar ions.

5.5 Thermophoretic deposition of SWNT thin films

In Publication IV, the small-scale TP was also used to deposit centimeter-scale thin films on Si/SiO_2 chips with lateral dimensions of ca. 1.5 × 1.5 cm, and to fabricate a test array of TFTs identical to the one used in Publication II.

The uniformities of the deposited SWNT films were evaluated from nine SEM micrographs obtained at the center and edges of a 1 cm² square located in the center of the chips. An illustration of the micrograph locations on the substrate is shown in Figure 5.5.1a. To facilitate the measurement of the SWNT density, the area density (μm⁻²) was approximated by the linear density (μm⁻¹), measured by detecting peaks in the greyscale values of the SEM scanlines. An example of an analyzed scanline is shown in Figure 5.5.1b. When deposition was carried out using a volumetric flow rate of 80 cm³/min through a 0.5 mm × 2 cm × 5 cm channel, defined by the cuts in the flow guide plates, a film with high spatial uniformity in the central 1 × 1 cm
of the substrate was obtained, and the SWNTs were measured to be randomly oriented. Deposition using a higher volumetric flow rate of 300 cm$^3$/min through an identical channel resulted in a non-uniform SWNT density with comparably fewer SWNTs observed along the centerline of the measured area, and a non-uniform angular distribution with the SWNTs aligned preferentially parallel to the flow direction (corresponding to an angle of 0 in the histograms and the vertical axis in the micrographs of Figures 5.5.1c and 5.5.1d). The spatial density distributions of films deposited using the two volume flow rates, expressed by the SWNT linear densities, and the orientation distribution of the SWNTs in each of the micrographs, are presented in Figure 5.5.1c and 5.5.1d. The magnitude of the alignment was quantified using the 2D order parameter $S_{2D}$, defined in Eq. 4.8.3. The results indicate that the small-scale TP design introduced in Publication IV can be used to deposit centimeter-scale uniform thin films of SWNTs or other aerosol-synthesized nanomaterials using a relatively low flow rate, which also corresponds to a near-unity deposition efficiency according to Eq. 5.4.2. The observed alignment suggests that SWNTs undergoing thermophoretic deposition can in principle be aligned using a lateral shear flow and are likely to maintain a position that is perpendicular to the temperature gradient during their deposition in a rectangular plate-to-plate TP channel.

The collection efficiency of the small-scale TP was also evaluated by comparing the densities of deposited SWNTs measured from SEM micrographs against the prediction given by Eq. 5.3.1, using the average of number concentrations measured before and after the deposition as $C$, and assuming that the effective deposition area $A$ corresponded to the 50 mm × 20 mm area between the inlet and outlet tubes, shown in Figure 4.4.1. To keep the deposited SWNT film uniform, volumetric flow rates below 100 cm$^3$/min were used, and the deposition efficiency $\eta$ was estimated by Eq. 5.4.2, using the experimentally observed value of $v_{tb}$ (35% of Eq. 3.4.4). The predicted and measured SWNT densities were found to match well, as shown in Figure 5.5.2.
Figure 5.5.2. Measured SWNT density vs. predicted density using Eqs. 5.3.1 and 5.4.2., using the experimentally observed value of $v_n$ (35% of Eq. 3.4.4), and representative SEM micrographs similar to those used in the density measurement. The scale bars are 2 μm long in all micrographs. The vertical error bars indicate the experimental error, resulting mainly from shift in aerosol concentration during the deposition. The horizontal error bars indicate one standard deviation and the vertical error bars indicate uncertainty caused by the measurement of the number concentration $C$. The red dashed line is to guide the eye. Copyright American Chemical Society, used with permission.

The fabricated TFTs exhibited uniform electrical properties across the centimeter-scale array, and out of 644 fabricated and measured devices, only one showed abnormal operation considering its channel dimensions, indicative of a defect in the substrate dielectric unrelated to the deposition process. The transfer curves of devices with $L_{CH} > 30$ μm are shown in Figure 5.5.3a. The best performing devices with dimensions $L_{CH} = W_{CH} = 100$ μm exhibited field effect mobilities exceeding 300 cm²/Vs, while simultaneously having an $I_{ON}/I_{OFF}$ ratio in excess of $10^6$, and typical devices with $L_{CH} > 30$ μm exhibited charge carrier mobilities of 50–100 cm²/Vs while simultaneously having $I_{ON}/I_{OFF}$ ratios between $10^4$ and $10^6$. A scatter plot of the field effect mobility versus the $I_{ON}/I_{OFF}$ ratio is shown in Figure 5.5.3b, and the output curves of a representative $W_{CH} = 100$ μm, $L_{CH} = 100$ μm device, showing saturation behavior, are shown in Figure 5.5.3c. The high field effect mobility and $I_{ON}/I_{OFF}$ values represent some of the best metrics obtained for SWNT TFTs fabricated from unsorted SWNTs, and indicate that the high performances demonstrated by Sun et al.100, 104 are not a result of the filter transfer process used in them, but rather indicative of the high quality of the FCCVD SWNTs, since similar or superior performance can be achieved using deposition by TP.

The values of $I_{ON}$ exhibited by the thermophoretically fabricated TFTs in Publication IV, shown in Figure 5.5.3d for devices with $L_{CH} > 30$ μm, were approximately four times higher than the corresponding values in Publication II, which could partially result from a higher mean SWNT diameter (1.1 nm in Publication II, 1.2 nm in Publication IV) leading to lower Schottky barriers between the SWNTs, but also from the cleaner surfaces of the thermophoretically deposited SWNTs, since SWNTs transferred by filter dissolution tend to be contaminated by poorly soluble remnants of the nitrocellulose filter. In contrast to this, based on the AFM micrograph of a finished device channel shown in Figure 5.5.3e, the surfaces of SWNTs deposited by TP were observed to be clean of any discernible contamination after the lift-off of the photoresist defining the channel area. Thus, the high TFT performance achieved in Publication IV may be viewed as an improvement over the results obtained in Publication II, and the deposition method is less prone to error than the filter dissolution method, in which trapped air bubbles or unintentional agitation of the sample during transfer may result in non-uniformities. In practice, access to FCCVD SWNTs with a clearly enriched semiconducting fraction would be however needed to improve significantly on the performance achieved in Publication IV, or to utilize the deposition method in the fabrication of functional large-scale circuits based on SWNT TFTs. Since the clean interfaces seemingly improve the contact resistances within the TFT channel, performances suitable for the applications discussed earlier
could, however, be achieved even with a slightly lower level of enrichment, such as a 90-95% fraction of semiconducting SWNTs.

**Figure 5.5.3.** Electrical characterization and atomic force microscopy (AFM) and SEM micrographs of TFTs fabricated using the small-scale TP in **Publication IV**. a) Transfer curves of devices with 100, 50, and 40 μm channel lengths and 500, 200, and 100 μm channel widths. b) Scatter plot of device field-effect mobilities and on/off ratios. c) Output curves of a representative LCH = 50 μm, WCH = 100 μm device, exhibiting saturation behavior. d) Histograms of Ion (measured at VDS = −10 V and VDS = −1 V and normalized to channel width) of devices with channel lengths 40, 50, and 100 μm. e) AFM (scale bar 1 μm) micrograph of SWNTs in a finished device channel and SEM (scale bar 10 μm) micrograph of the entire channel. Copyright American Chemical Society, used with permission.

In **Publication V**, a scaled-up TP design, presented in Figure 4.4.2, was presented and used to directly deposit SWNT TCFs on glass and PET substrates. Based on number concentration measurements using a CPC, shown in Figure 5.5.4a, the deposition efficiency of the design is high, and the number concentration of the SWNT aerosol synthesized by a FCCVD reactor was observed to decrease by approximately 97.5% when measured through the scaled-up TP with a temperature gradient of $9.3 \times 10^4$ K/m applied, both when the substrate was held stationary and when it was oscillated in accordance with Figure 4.4.2c. The spatial uniformity of the deposited SWNT thin films was evaluated based on SEM of near-monolayer films on 50 mm Si/SiO$_2$ wafers. As in **Publication IV**, the density of the SWNTs was determined by approximating the area density (in units of μm$^{-2}$) by the linear density (μm$^{-1}$) determined by analysis of SEM scanlines. When no temperature gradient was applied, a few individual SWNTs (none or a few in a SEM micrograph of 57 μm x 43 μm), most likely carried on the surface by diffusion, were observed. This indicates that in the geometry studied, SWNTs and particles with similar or smaller aerodynamic diameters should not deposit by inertial impaction. The SWNT deposition pattern on a 50 mm Si/SiO$_2$ wafer, held stationary at a distance of 0.75 mm from the hot plate orifice of the TP, is shown in Figure 5.5.4b. The observed SWNT density decreases as a function of the distance from the orifice, and practically no SWNTs were observed more than 10 mm away from it. When the wafer was oscillated below the orifice, a highly uniform coating of SWNTs was observed. The measured SWNT density, shown in Fig. 2b, was found to be
within 20% of its average value across the entire wafer. The source of the non-uniformity is most likely a slight tilt between the stage and the hot plate, which are difficult to align completely in the academic facilities the TP has been built in, and may change the distance between the substrate and the hot plate significantly when using 279 μm thick Si/SiO₂ or 500 μm thick borosilicate glass wafers as substrates, since the substrate thickness is more than a third of the intended distance between the hot plate and the surface of the substrate.

Like in Publication IV, the SWNTs deposited using the scaled-up TP were observed to orient themselves with the flow to some extent, and the average orientation was found to point away from the hot plate orifice. A map of orientation distributions measured from micrographs on a stationary wafer and two representative orientation distributions are presented in Fig. 5.5.4d. The magnitude of the orientation was quantified using the 2D order parameter S₂D defined in Eq. 4.8.3. On a wafer that was oscillated under the orifice in accordance with Figure 4.4.2c, slightly weaker orientations, shown in Figure 5.5.4e, were observed.

The flow and temperature fields inside the scaled-up TP were also investigated using computational fluid dynamics and heat transfer simulations, carried out in the geometry and mesh presented in Figure 4.10.2. A plot of the simulated velocity field between the substrate and the hot plate is presented in Fig. 5.5.5a. The SWNT orientation distributions measured at different
points on a stationary wafer, presented in Figure 5.5.4d, matched the direction of the simulated velocity field shown in Fig. 5.5.5a well. The slightly diminished orientation on the oscillated wafer is also easy to understand in light of the velocity field, since during oscillation, each point on the wafer spends time far from the orifice, where the flow velocity is significantly smaller. The match between the measured orientation distributions and the simulated velocity field indicates that the simulated velocity field is realistic, and similar modelling can be used to scale the design up for larger substrates or flow rates. As previously noted by Holunga et al.\textsuperscript{156}, heating of the inlet gas flow of a TP may be necessary at higher volume flow rates to prevent convective heat transfer by the carrier gas from disturbing the temperature field inside the TP. A plot of the temperature field on a cross-sectional plane, located at the symmetric boundary of the mesh, is shown in Figure 5.5.5b. Based on the simulation, the hot gas exiting the orifice will disturb the otherwise constant temperature gradient between the hot plate and the substrate by a small but discernible amount. However, based on the simulations, at the temperatures, volume flows and geometry used, the ambient-temperature gas entering from the inlet has time to reach the hot plate temperature before entering the orifice, indicating that heating of the inlet parts of the TP is not necessary.

To demonstrate the applicability of the thermophoretically deposited SWNT coating as TCFs, visible thin films were deposited on 50 mm borosilicate glass wafers with a thickness of 500 μm, and 50 × 50 mm sheets of poly(ethylene terephthalate) (PET), with a thickness of 100 μm. The deposited TCFs on borosilicate glass were doped by drop casting HNO\textsubscript{3} on the film, similarly to the films in \textbf{Publication III}. Interestingly, HNO\textsubscript{3} had no effect on films deposited on PET, on which the solution visibly beaded into near-spherical droplets and could not wet the SWNT coating. Instead, a 16-mM solution of AuCl\textsubscript{3} in acetonitrile was used. For comparison of TCF performances obtained with different deposition methods, SWNT thin films were also collected from the same synthesis process using filtration, press transferred on quartz windows and smaller PET sheets and doped using the same solutions. Plots of the TCF sheet resistance and optical transmittance at 550 nm on glass and PET substrates are presented in Figure 5.5.5a and 5.5.5b. The press transferred TCFs performed as expected, given their mean bundle length of 7.6 μm and a concentration close to the medium concentration condition in \textbf{Publication}...
III, and a sheet resistance of approximately 100 Ω/sq. after HNO₃ doping, at an optical transmittance of 90% measured at 550 nm was achieved. A fit of the experimental data from press transferred films to Eq. 2.5.3, or the figure of merit $K$, is included in the figures to facilitate comparison of the deposition methods. Before doping, TCFs deposited by TP showed slightly lower sheet resistances than the press transferred TCFs both on glass and PET, which could either result from the measurement protocol used or from a morphological difference between the TCFs collected using different methods. Due to the larger number of measurements carried out per sample, the TCFs deposited by TP are exposed to atmospheric dopants such as oxygen and water for a longer time, which can lead to a decreased sheet resistance. Morphological differences are hard to discern given the disordered structure of the films, but when depositing by TP, the pristine SWNT film could be assumed to be more tightly packed, since on the filter, the top layer of already deposited SWNTs acts as an extension of the filter membrane and prevents the SWNT aerosol from reaching its surface, thus forming a more three-dimensional structure. After doping, TCFs deposited using press transfer exhibited a slightly better performance on glass substrates, which could result from an uneven doping level caused by the difficulty of applying the HNO₃ solution evenly on a larger substrate. Meanwhile, on PET, TCFs deposited using the TP exhibited on average a 20% better performance, which is also competitive with conventional TCF materials on polymer substrates. Again, as in Publication IV, this suggests that the high TCF performance obtained using FCCVD SWNTs is not a result of the filter-based deposition method, but rather stems from the intrinsic quality of the material.

The observed variation in the properties of thermophoretically deposited TCF on glass shows similar variation as the density observed by SEM, and the absorbance and reciprocal sheet resistance, which can be assumed to be linearly dependent on the SWNT density, of all data points measured from the same wafer fit within ±20% of their averages. Meanwhile, the spatial variation was much lower, approximately ±7%, in the case TCFs deposited on PET. This could result from the fact that the PET sheets are significantly thinner than the borosilicate glass wafers, and a possible misalignment of the sample stage, mentioned before, thus has a lesser effect on the flow. Evaluation of the deposition uniformity on PET by SEM was not carried out, since the imaging of near-monolayer SWNT films on a thick insulator is complicated by substrate charging. Finally, the limited alignment ($S_{2D}$ typically between 0.2 and 0.3) observed on the uniformly coated wafers in did not result in any anisotropicity in the sheet resistance that could be measured using the four-point probe used. Each reported value of the sheet resistance in Figure 5.5.5 was the average of ten consecutive measurements carried out using two probe orientations, and in all positions on the wafers and PET sheets except a few outliers, rotating the four-point probe by 90 degrees did not result in a difference that was larger than the standard deviation of measurements carried out at the same location using just one orientation of the probe. The mechanisms of the flow-induced SWNT alignment and possible ways to further increase it are discussed briefly in Chapter 5.6.
Figure 5.5.5. a) Sheet resistance vs. transmittance at 550 nm of thermophoretically deposited (red triangles) and press transferred TCFs (blue circles) on glass. The open symbols indicate pristine samples and filled symbols indicate HNO₃ doped samples. b) Sheet resistance vs. transmittance at 550 nm of thermophoretically deposited (red squares) and press transferred (blue circles) TCFs on PET. The open symbols indicate pristine samples and filled symbols indicate AuCl₃ doped samples. The blue curves are fits of Eq. 2.5.3 to the press transferred film data (dashed curve corresponding to data from pristine samples, solid curve to data from doped samples) c) Representative visible transmission spectra from a TCF on glass, recorded at five different points on the substrate and on PET, recorded at nine different points on the substrate. The approximate measurement points are shown in g). d) Representative SEM micrograph of a pristine SWNT film with an optical transmittance of ca. 94%, deposited by TP on borosilicate glass. e)-f) Photographs of TCFs on a 50-mm borosilicate wafer and a 50 mm × 50 mm PET sheet. g) Approximate locations of the measurements on the glass wafers and the PET sheets. The dashed rectangles correspond to the spectrophotometer spot size of 5 mm × 10 mm.

5.6 Discussion and directions for future research

In Publication I, the diffusive transport and agglomeration of an SWNT aerosol were studied mainly from the viewpoint of TCF performance, although the obtained effective diameter, most likely a convolution of the mobility and effective collision diameters as discussed in Chapter 5.1, can be used as a starting point when considering e.g. diffusive losses or deposition. Since the obtained values can be treated as lower bounds based on the argument outlined in Chapter 5.1, their use will at worst lead to overestimation of losses or deposition rates. The experimental setup used in Publication I could also be used with other types of FCCVD SWNTs, which could be particularly enlightening when using processes that produce SWNT with significantly shorter or longer mean lengths. As pointed out earlier, the equivalent-mobility diameter determining diffusive transport and deposition could be also determined using e.g. diffusion batteries with suitable dimensions, and the correspondence between it and the SWNT or bundle dimensions could be studied by measuring size distributions deposited before and after the battery.

The correlation between the electrical mobility diameter \(d_{ME}\) and the physical dimensions of an SWNT could be evaluated using the processes described in this work, since published experimental data, and the models used to interpret it, do not cover the dimensions of the individual or slightly bundled SWNTs synthesized here. This could be carried out by using a DMA
to sort the SWNT by different \(d_{ME}\) and measure the length and bundle size distributions corresponding to each \(d_{ME}\) similarly to the measurements in Publication I. A correlation between \(d_{ME}\) and the SWNT or bundle length could in principle be utilized to improve TCF performance by removing shorter SWNTs from the reactor effluent by a low-pass electrostatic filter that deposits SWNTs with electrical mobility diameters below a given value. In practice, however, the alignment of SWNTs in an electric field may diminish the dependence of \(d_{ME}\) on the SWNT length, and as an illustrative example, the number size distributions of SWNTs with different lengths and diameters but very close mean \(d_{ME}\), measured in Publication IV, are presented in Figure 5.6.5. Additionally, the charging states of unbundled SWNTs could be evaluated based on tandem DMA measurements similar to those carried out earlier by Nasibulin et al. using shorter, bundled FCCVD SWNTs\(^{167}\).

![Figure 5.6.5](image)

**Figure 5.6.5.** Number size distributions for three SWNT populations from Publication IV, measured by an SMPS+C system.

In Publication IV, it is proposed that the thermophoretic sampling method could be used to fabricate mixed-dimensional van der Waals heterostructures with very clean interfaces, consisting of SWNTs on the surface of a two-dimensional material such as graphene, hexagonal boron nitride, or two-dimensional metal dichalcogenides\(^{191}\). At the moment of writing, the interfacial physics of such structures are under active research and could be utilized in novel photonic and electronic devices. The scaled-up TP presented in Publication V could be also used to deposit SWNT TCF contact layers on challenging or fragile substrates not suited for press transfer, such as nanowire arrays or mesoporous materials. The systems presented in Publication IV-V are also not limited to the deposition of FCCVD SWNTs, and could also be used to deposit other functional coatings consisting of aerosol synthesized nanomaterials.

The semi-empirical model introduced in Publication I can be used to select which parameters to improve when developing new FCCVD processes for the deposition of TCFs. While the performance limit of 25 \(\Omega/\text{sq.}\) at a 90% transmittance postulated in Publication I seems to be unlikely to be surpassed by just improving the SWNT dimensions, \(i.e.\) increasing the length or decreasing the bundle diameter, a radically different approach, such as the micro-patterning technique developed by Fukaya et al. and used in Publication III, could in principle be used to reach the value without having to use a very low concentration to completely eliminate bundling. Another route to beating the predicted limit could be to align the SWNTs, since many applications using TCFs do not necessarily need an isotropic sheet resistance. While this could be carried out \(e.g.\) by using local electrostatic forces, using them would require the fabrication of microelectrodes on the TCF substrate, and in practice a stronger flow-induced alignment would be preferable. A further development of the scaled-up TP in Publication V, with higher shear rates, could be used to deposit even more aligned films with possibly anisotropic sheet resistances. Alternatively, even the presented system could possibly be used deposit more
aligned films if significantly longer FCCVD SWNTs become available. Briefly, the shear-induced alignment of fibers is expected to be proportional to the rotational Péclet number $Pe$, describing the ratio of hydrodynamic and Brownian forces,

$$Pe = \frac{\dot{\gamma}}{D_r}$$  

(5.6.1)

where $\dot{\gamma}$ is the shear rate and $D_r$ is the rotational diffusion coefficient, which is for long, thin rods$^{125}$

$$D_r = \frac{3k_BT}{\pi \mu \beta l^3} (\ln 2\beta - 1.4),$$  

(5.6.2)

where $l$ is the length and $\beta$ is the aspect ratio of the rod, and the numerical constant 1.4 is valid for $\beta > 10$. In practice, careful attention should be paid to the flow design of a hypothetical higher-flow TP, since local eddies or turbulence may lead to the formation of loops or curls of SWNTs.

The controlled synthesis and deposition methods outlined in this dissertation provide a straightforward route to the deposition of clean, individual SWNTs on practically any flat substrate. This facilitates the quick and easy measurement of SWNT size distributions, which, in combination with the semiempirical models proposed in Publication I, aid in the characterization and development of the floating catalyst CVD method. Thermophoretic deposition also opens new possibilities for the characterization of FCCVD SWNTs, since samples can be easily prepared for e.g. micro-Raman measurements of individual, separated SWNTs, photoluminescence spectroscopy of air-suspended SWNTs similar to those pictured in Figure 2.2.4, or Rayleigh scattering spectroscopy$^{192}$. Since samples suited for chirality measurements by electron diffraction can be collected simultaneously, this provides a route for the evaluation of the validity spectroscopic methods against a calibration-free measurement of the SWNT chirality distribution. At the time of writing, a study using this principle to evaluate the validity of SWNT electronic type fractions measured by micro-Raman measurements, by comparing them to chirality distributions obtained by electron diffraction has been accepted for publication. Obtaining a suitable density for such measurements is further facilitated by the CPC-based concentration measurements used in Publications II and IV.
References


Brady, G. J.; Way, A. J.; Safron, N. S.; Evensen, H. T.; Gopalan, P.; Arnold, M. S., Quasiballistic carbon nanotube array transistors with current density exceeding Si and GaAs. Science advances 2016, 2 (9), e1601240.


Corrigendum for Publication I

In Publication I, Equation 1 has been misprinted. The correct equation is

\[ K = \frac{\sigma_{DC}}{A} = - \frac{1}{R_s \ln T}. \]  \hspace{1cm} (1)

All values of \( K \) reported in the publication have been calculated using the correct equation.
Thermophoretic and diffusive gas-phase transport of single-walled carbon nanotubes and their applications in thin film electronics

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