Production and Deposition of Well Defined Aerosol Nanoparticles for Studies of Basic Properties

Thesis by Christian Peineke
Production and Deposition of Well Defined Aerosol Nanoparticles for Studies on Basic Properties

Proefschrift

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aan de Technische Universiteit Delft
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Prof. dr. ir. J.T. Fokkema,
voorzitter van het College voor Promoties,
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Production and Deposition of Well Defined Aerosol Nanoparticles for Studies on Basic Properties

Thesis

presented for the degree of doctor
at Delft University of Technology
under authority of the Vice-Chancellor,
Prof. dr. ir. J.T. Fokkema,
Chairman of the Board of Doctorates,
to be defended in public in the presence of a committee on

Wednesday, March 26th, 2008 at 15 o’clock

by

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Stellingen

Behorend bij het proefschrift

"Production and Deposition of Well Defined Aerosol Nanoparticles for Studies on Basic Properties"

door

Christian PEINEKE

1. Een schoon aerosol-deeltje is een tegenspraak.

2. Nanotechnologie maakt gebruik van schaaleffecten. Daarom zou een nanodeeltje door het optreden van schaaleffecten gedefinieerd moeten worden in plaats van grootte alleen.

3. Mathematische juistheid wordt vaak in ruil voor duidelijkheid overboord gegooid. Het plotten van \( \frac{dN}{d \log(dp)} \) tegen \( dp \) om een deeltjesgrootteverdeling te tonen, mist allebei.


5. “Een experiment is een vraag aan de natuur. Alleen als we de goede vragen stellen kunnen we het antwoord begrijpen”⁷. En toch blijft het antwoord altijd dieper dan we denken.

6. Een ingenieur is iemand die de problemen van vandaag oplost. Een wetenschapper is iemand die problemen oplost, die op het moment nog niemand heeft.

7. Als de evolutie alleen ingenieurs zou voortbrengen, zouden we vandaag in perfecte grotten rond perfecte kampvuren leven.

8. Er zijn drie philosophische problemen die geen oplossing hebben.
   - De vraag van de kip en het ei: Wat was er eerst?
   - Het bewijs dat iets niet bestaat.
   - Het bewijs dat god bestaat.

9. In een maatschappij leidt de afwezigheid van bedreiging tot anarchie.

Deze stellingen worden opponeerbaar en verdedigbaar geacht als zodanig goedgekeurd door de promotor, Prof. Dr. A. Schmidt-Ott
Propositions

Adjunct to the thesis

"Production and Deposition of Well Defined Aerosol Nanoparticles for Studies on Basic Properties"

by

Christian PEINEKE

1. A clean aerosol particle is a contradiction in itself.

2. Nanotechnology uses size effects. Hence, a nanoparticle should be defined through the occurrence of size effects rather than size alone.

3. Mathematical correctness is often abandoned for the sake of clarity. The custom to plot $\frac{dN}{d\log(dp)}$ vs. $dp$ as representation of a size distribution, however, lacks both.

4. Advantages are always opposed by disadvantages. Engineering means to choose tolerable disadvantages.

5. "An experiment is a question to nature, but only if we ask proper questions we are able to understand the answer"1. Nevertheless, the answer is always more complex than we think.

6. An engineer is somebody solving today’s problems, a scientist is somebody solving problems nobody has, yet.

7. If evolution would have bred only engineers we would be living in perfect caves around perfect fires.

8. There are three philosophical key issues, which can never be solved.
   - The question of the egg and the chicken: Which one was first?
   - The proof of non existence.
   - The proof that god exists.

9. In a society the absence of a threat leads to anarchy.

These propositions are considered opposable and defensible and as such have been approved by the supervisor, Prof. Dr. A. Schmidt-Ott

---

1R. Kleckers, physics teacher
To my Late Grandfather
Preface

It is in the nature of PhD research to be very specialized and it is not aim of the written report to be comprehensive with respect to introductory explanations. Although I can strongly recommend to read the whole thesis I am aware that only few readers might be interested in the detailed work and that most likely the majority of the printed thesis ends up catching dust on a bookshelf. Hoping to produce a somewhat more useful book, this thesis is basically separated into two sections. The chapters, which contain the scientific results and the appendices, which are a collection of notes on background information and problems encountered during the course of this thesis. They give more detailed information on some of those topics which are fundamental to aerosol science, but often not explained sufficiently in introductory textbooks or on course level. Their content compiles the bits and pieces from different sources into a more or less readable text and points out some of the "inaccuracies" found in the printed papers. After all, the way in which these chapters are written is rather personal and represents a physics oriented view of the matter, i.e. that many of the notes have a tendency towards mathematics. The latter section is meant to be useful for students starting to work in the lab or who just need a different view on the topic.

Hopefully the copies of the thesis are more than just dusted off and contribute to better understanding of aerosols and help to promote aerosol technology in R&D and in industrial environments.

Christian Peineke
Delft, March 2008
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List of Symbols

\( \Delta H_s \)  \hspace{1cm} \text{Latent heat of evaporation}
\( \alpha \)  \hspace{1cm} \text{Fraction of ionized particles (surface charging)}
\( \alpha_{coll} \)  \hspace{1cm} \text{Collision parameter}
\( \alpha_a \)  \hspace{1cm} \text{Momentum accommodation coefficient}
\( \beta \)  \hspace{1cm} \text{Charging efficiency (surface charging)}
\( \delta \)  \hspace{1cm} \text{Diameter of Fuchs' adsorption sphere}
\( \delta_g \)  \hspace{1cm} \text{Collision diameter of carrier gas}
\( \epsilon_0 \)  \hspace{1cm} \text{Permittivity of free space, } \frac{\mu_0}{4\pi c^2} = 8.854 \cdot 10^{-12} \text{AsV}^{-1} \text{m}^{-1}
\( \epsilon_r \)  \hspace{1cm} \text{Complex dielectric constant of a material}
\( \eta \)  \hspace{1cm} \text{Dynamic viscosity of a medium, } 1.83245 \cdot 10^{-5} \text{Ns/m} \quad [1]
\( \eta_{pe}^{q-(q+1)} \)  \hspace{1cm} \text{Emission coefficient for photoionization}
\( \eta_{ia}^{q \pm q \pm 1} \)  \hspace{1cm} \text{Ion attachment coefficient for negative and positive ions respectively}
\( \eta_g \)  \hspace{1cm} \text{Viscosity of gas (air = } 1.81 \cdot 10^{-5} \text{Ns/m}^2)\)
\( \gamma \)  \hspace{1cm} \text{Specific heat ratio of carrier gas}
\( \kappa_{GD} \)  \hspace{1cm} \text{Transmission coefficient of the glass electrode at light frequency } \nu
\( \Lambda \)  \hspace{1cm} \text{Geometric factor of a DMA, see equation (A.3), page 130}
List of Symbols

\( \lambda \)  
Particle mean free path, 67.3nm for air at standard conditions [1]

\( \lambda_{ion} \)  
Ion mean free path

\( \lambda_{acc} \)  
Accommodation coefficient

\( \nu \)  
Frequency of light

\( \Phi \)  
Electric potential

\( \psi^q \)  
Probability for a particle to be in charge state \( q \)

\( \varphi^{q-(q+1)} \)  
Effective work function of a particle

\( \varphi_{ec} \)  
Electronic work function of bulk material in vacuum

\( \rho_{pe}^{q-(q+1)} \)  
Photoelectron emission rate

\( \rho_{ia}^{q=q+1} \)  
Attachment rate for ions by diffusion

\( \rho_g \)  
Density of gas (air = 1.2 kg/m\(^3\))

\( \rho_p \)  
Particle density

\( \sigma \)  
Geometric mean deviation of a distribution

\( \tau \)  
Residence time of a particle in a DMA

\( \xi \)  
Position of a measurement (x-value)

\( \zeta \)  
Electrical mobility (variable of integration)

\( a, b, c \)  
Constants in Cunningham slip correction factor

\( a_i \)  
Molar fraction of i-th component

\( B \)  
Mechanical mobility of a particle

\( b_{min} \)  
Minimum tangential distance from particle center to the trajectory of an ion passing by [2]

\( b_{pe} \)  
Photoemission exponent, 2 for metals
\( \bar{c}_{\text{ion}} \) Mean thermal velocity of ions
\( c \) Speed of light 299792458 m/s
\( C_M \) Specifies a certain surface state
\( c_s \) Speed of sound = \( \sqrt{\frac{\gamma R T_1}{M}} \) with \( T_1 \) being the upstream temperature
\( d_a \) Aerodynamic diameter
\( d_c \) Characteristic length
\( d_p \) Mobility equivalent diameter
\( d_s \) Stokes diameter
\( d_v \) Volume equivalent diameter
\( d_{\text{cut}} \) Cutoff Stokes diameter corresponding to \( \text{Stk}_{50} \)
\( D_{\text{ion}} \) Ion diffusion coefficient
\( e \) Elementary charge \( 1.6022 \cdot 10^{-19} \text{C} \)
\( E, E_r \) Electric field strength (of a radial field)
\( g \) Gravity
\( g_a, g_i \) Number of angular momentum states for the atom and ion, respectively (surface charging)
\( h \) Planck’s constant \( 6.602 \cdot 10^{-34} \text{Js} \)
\( I \) Current
\( I_{ce} \) Photocurrent emitted from the center electrode
\( I_{\text{wire}} \) Current through a glowing wire
\( J_{ce} \) Current density of photoelectrons emitted from the center electrode of the GDMA
**List of Symbols**

\( \mathcal{J}_{\text{Photon}} \)  \hspace{1em} Photon flux density

\( J_+, J_- \)  \hspace{1em} Positive and negative current density, respectively

\( k_B \)  \hspace{1em} Boltzmann’s constant, \( 1.38 \cdot 10^{-23} \text{JK}^{-1} \)

\( K_c \)  \hspace{1em} Photoemission constant

\( Kn_p \)  \hspace{1em} Particle Knudsen number, \( Kn_p = \frac{2 \lambda}{d} \)

\( Kn_{\text{ion}} \)  \hspace{1em} Ion Knudsen number

\( l \)  \hspace{1em} Distance to the center of charge

\( L_{\text{DMA}} \)  \hspace{1em} Length between aerosol inlet and outlet in a DMA

\( L_{\text{Lamp}} \)  \hspace{1em} Length of a lamp

\( \dot{m}_g \)  \hspace{1em} Mass flow rate of carrier gas

\( \mathcal{M} \)  \hspace{1em} Measurement function as obtained from an instrument (y-values)

\( m_e \)  \hspace{1em} Electron mass

\( M_m \)  \hspace{1em} Molar mass

\( m_p \)  \hspace{1em} Mass of particle

\( m_{\text{gas}} \)  \hspace{1em} Carrier gas mass

\( m_{\text{ion}} \)  \hspace{1em} Ion mass

\( N' \)  \hspace{1em} Particle size distribution after all corrections

\( N \)  \hspace{1em} Particle concentration

\( n_{\text{ion}}^\pm \)  \hspace{1em} Concentration of positive/negative ions

\( n_+ \)  \hspace{1em} Number of positively charged particles

\( n_0 \)  \hspace{1em} Number of neutral particles

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$N_a$ Avogadro’s number $6.0220453 \cdot 10^{23}$

$N_{CM}$ Particle concentration of particles with surface state $C_M$

$N_{q,C_M}$ Number of particles with charge $q$ and chemical composition $C_M$

$N_{q,d_p}$ Concentration of particles with charge $q$ and diameter $d_p$

$\mathcal{O}$ Object function (original data)

$p$ Pressure

$p_0$ Partial pressure of a substance

$p_1$ Upstream pressure of carrier gas.

$P_s$ Saturation vapor pressure

$P_{abs}$ Photon absorption efficiency

$p_{ion}$ Ion polarity ($\pm 1$)

$P_{Lamp}$ Power of light emitted by a lamp at photon energy $h\nu$

$P_{wire}$ Heating power of a glowing wire

$\bar{q}_t$ Time average mean charge of a single particle

$\bar{q}_q$ Charge state average mean charge

$q$ Number of elementary charges

$Q_i$ Flow through impactor

$q_p$ Particle charge $q_p = e \cdot q$

$Q_{excess}$ Excess-gas flowrate

$q_{max}$ Maximum number of charges obtained by a particle

$q_{min}$ Most negative charge obtainable by a particle

$Q_{mono}$ Monodisperse aerosol flowrate
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{poly}}$</td>
<td>Polydisperse aerosol flowrate</td>
</tr>
<tr>
<td>$Q_{\text{sheath}}$</td>
<td>Sheath-gas flowrate</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial position of a particle</td>
</tr>
<tr>
<td>$r_a, r_i$</td>
<td>Outer and inner radius of a cylindrical DMA</td>
</tr>
<tr>
<td>$r_i$</td>
<td>Evaporation rate of an adsorbate</td>
</tr>
<tr>
<td>$r_{m/\text{radot}}$</td>
<td>Molar/total evaporation rate</td>
</tr>
<tr>
<td>$r_n$</td>
<td>Radius of aerodynamic lens or impactor nozzle.</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Particle radius</td>
</tr>
<tr>
<td>$r_{\text{aps}}$</td>
<td>Apsidal distance</td>
</tr>
<tr>
<td>$r_{L/DMA}$</td>
<td>Distance from the center of a lamp to the center of the annulus between the electrodes</td>
</tr>
<tr>
<td>$R_{\text{wire}}$</td>
<td>Resistance of a glowing wire</td>
</tr>
<tr>
<td>$Re_p$</td>
<td>Particle Reynolds number</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface</td>
</tr>
<tr>
<td>$Stk$</td>
<td>Stokes number</td>
</tr>
<tr>
<td>$T$</td>
<td>Transfer function of an instrument</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$U_i$</td>
<td>Ionization energy of an adsorbed atom/molecule</td>
</tr>
<tr>
<td>$U_{\text{DMA}}$</td>
<td>Voltage between inner and outer electrode of a DMA</td>
</tr>
<tr>
<td>$U_{\text{wire}}$</td>
<td>Voltage drop over a glowing wire</td>
</tr>
<tr>
<td>$v_e$</td>
<td>Impactor exit velocity</td>
</tr>
<tr>
<td>$v_s$</td>
<td>Settling velocity of a particle</td>
</tr>
<tr>
<td>$v_{el}$</td>
<td>Velocity of a particle due to electric fields</td>
</tr>
</tbody>
</table>
Relative velocity
Measurement variable
Photoyield for the emission of an electron from a particle with charge state \( q \)
Photoyield for the emission of electrons from the center electrode of the GDMA
Mean mobility extracted from the DMA
Width of the mobility band extracted by a DMA
Electric mobility of a particle
Ion electric mobility
Introduction

Wissenschaft
Einem ist sie die hohe, die himmlische
Göttin, dem anderen
Eine tüchtige Kuh, die ihn mit Butter
versorgt.²

(von Goethe [3])

The search for new materials and material properties has advanced to smaller and smaller structures during the past years. Inorganic particles in the size range below 100 nm are interesting for many applications, because on this scale properties often vary strongly from bulk. Due to confinement, electronic states are quantized which has a large impact on e.g. conduction, catalysis and photoemission. At this scale crystallographic configurations which are unstable on large scale become available, which leads to different mechanical and surface properties, e.g. in catalysis or for wear resistant coatings. The specific surface of nanostructured materials is very high as compared to bulk and diffusion length inside the particles are small, thus diffusion is fast e.g. for gas storage and sensing.

Nanoparticles are traditionally produced on large scale in wet chemical batch processes involving solvents. The surface of these particles is necessarily contaminated due to the very limited purities in which liquid

²Science - For the one it is the high, the devine goddess, for the other a capable cow that supplies him with butter.
Introduction

Solvents are available. The desired nanoparticles are often contaminated by the unwanted side products of the wet chemical reaction and must be cleaned in an additional process step.

Aerosol methods allow the production of much cleaner particles in a continuous process. Solvents are omitted and particles are only covered with a gas or water adsorption layer. Particle purity depends on the initial purity of the precursor material, e.g. a metallic wire or powder, and often additional refining is not necessary. Aerosol technology offers methods for direct determination of product properties as e.g. size, hygroscopicity, magnetic moment, particle density and many others. Aerosol size classification can be used to select a specific particle size for further applications. The production processes are continuous, so product properties can be controlled in-line and it is rather easy to switch to new process conditions, which result in different product properties.

Different stages of aerosol nanotechnology were investigated in this work which can be combined into a production line for nanotechnology devices or applied for quick material screening e.g. in catalyst research. The aerosols are produced by a glowing wire generator (GWG), which was characterized with respect to process conditions, choice of material, size limitations and particle charging (chapter 1). The latter is now understood and external chargers can be omitted. They pose an additional process step inevitably causing contamination of the products. Many applications require charged particles and e.g. the size distribution can be determined directly for process control, if the charging efficiency is known. The simplicity and material purity offered by this method are other key advantages.

In chapter 2 the feasibility of separating nanoparticles with respect to their shape and surface morphology based on basic properties is investigated. A prototype of a separation stage was built earlier by Kirsch [4] and applied for the separation of different materials and material shapes. While the separation of different materials is understood, the mechanisms leading to the separation of particles with respect to shape remained unclear. In the current work previous experimental results were reproduced and models were developed to simulate the separation process of particles with different shape. The models were successfully applied on the separation of aggregates and round particles, which was observed in the experiments. The separation of nanoparticles with well defined surfaces
is needed for many applications, e.g. to better understand the underlying chemical mechanisms in catalysis.

Chapter 3 describes how nanoparticles generated from aerosol processes are used to study basic catalytic properties of the material. Nanoparticles were deposited on a surface to investigate catalytic reactions under the influence of an electric field. Microreactor methods were applied in combination with highly efficient product detection (mass spectroscopy) on small amounts of catalyst material, which reduces cost and the risk of hazardous chemicals and situations. The use of micrometer sized structures makes it possible to generate strong electric fields that were used to alter the electronic structure of the catalyst and study the effect on catalytic activity. The electric field can be varied easily and so can the properties of the catalyst, which is a first step towards tunable catalyst devices. Combined with the flexibility of aerosol processes to produce clean and well defined particles these microreactor systems can be used for quick screening of materials. The use of a substrate to support the catalyst material introduces uncontrollable interactions between the materials, e.g. by the substrate surface structure or contact potentials. To eliminate these effects nickel aerosol particles were used directly as catalyst for the methanation of carbon monoxide. Particles were selected according to their charge and the influence of the charge state on the activation energy of the reaction was studied.

Besides the application of aerosol nanoparticles for the study of basic properties the present study investigated the viability of nanoparticle deposition by focused impaction for the production of new materials and sensor devices. In chapter 4 is described how aerosol technology is used for the production of porous, nanostructured, metallic structures on micrometer scale for sensor applications. The conductivity of this material is studied under the influence of an atmosphere containing hydrogen, which made it possible to extract basic information on particle sintering and proved the concept of an ultrafast, nanoparticle based hydrogen gas sensor. It was shown, that current can be specifically used to induce sintering in deposited nanostructured material, which alters the behavior of the material.

The investigated methods are versatile and can be used in different combinations alone or with other aerosol instrumentation to assemble process lines, either for scientific purposes, quick product development or com-
Introduction

plete device fabrication. The detailed understanding of the different components makes it possible to tailor the different process steps for specific product properties and feedback of online analysis can be used for process control. The demonstration of usefulness and versatility of aerosol processes for science, R&D and production is a step towards the large scale integration of aerosol techniques in nanotechnology, besides the production of few bulk chemicals such as fumed silica, titania or carbon black.
Chapter 1.

The Glowing Wire Generator

She went on: “Would you tell me, please, which way I ought to go from here?” “That depends a good deal on where you want to get to,” said the Cat. “I don’t much care where” said Alice. “Then it doesn’t matter which way you go,” said the Cat. “as long as I get SOMEWHERE,” Alice added as an explanation. “Oh, you’re sure to do that,” said the Cat, “if you only walk long enough.”

(Carroll [5])

Surface contamination has an impact on electronic, optical, electrical, magnetic, chemical, and mechanical properties. The size-effects and the critical influence of the outermost atomic layer including adsorbates arise from the confinement and quantization of conduction electrons within a small volume and the high surface-to-volume ratio. There is therefore a need for a clean particle production principle. Here, aerosol methods are generally superior to liquid phase routes, because in the latter case the
Chapter 1. The Glowing Wire Generator

purity is less controllable and surfactants are unavoidable. Adsorbate-free surfaces are essentially restricted to ultra-high vacuum experiments, but one former study [6] has proven, that adsorbate-free nanoparticle surfaces can be obtained when ultra-clean gas is used and when only the material to be evaporated is heated in the evaporation-condensation particle production process. This study applied the glowing wire method. Starting out with clean particles, gas-particle interactions, e.g. adsorption and catalytic reaction can be studied, as demonstrated in the publication cited above.

Many applications based on small quantities of nanoparticles with a diameter of less than some tens of nanometers such as gas sensors [7] and optoelectronic devices rely on a source delivering a reproducible size, electrical charge and concentration during e.g. manufacturing of devices. For fundamental studies on the nanoparticle properties high purity of the particle surface is further required.

The glowing wire generator (GWG), where material is evaporated from a resistively heated wire and subsequently quenched by a gas stream, has been introduced by Schmidt-Ott et al. [8] and applied for the production of metallic particles for research purposes since then [6, 9–12]. However, up to now no detailed study of the method was published and the potential of the method of producing high concentration monodisperse spherical nanoparticle aerosols has not been realized. The fact that a significant fraction of the formed particles is charged is of special interest, since the aerosol is directly usable for size classification and analysis via electric mobility without additional charging, as shown by Fernandez de la Mora et al. [11].

Size distributions of particles produced by a glowing wire were measured for silver, palladium, zirconium and niobium. For silver and palladium the total particle production as well as the amount of self-charged particles were determined for different flow rates. Different purities of silver wires were used. The influence of the wire temperature was studied on palladium. Due to the extremely high supersaturations in the metal vapors, the system is far from equilibrium and traditional nucleation and condensation theories are not applicable. It was assumed that collision leads to sticking, already at the atomic scale, so that Brownian coagulation represents a valid model for the growth of the particles from the very beginning. It leads to the self-preserving log-normal size distribution [13].
1.1. Principle of Operation

The group of Castleman and Khanna has shown that according to quantum mechanics, atomic clusters behave like "superatoms" [14]. This means that they have electronic states resembling those of atoms and corresponding chemical properties. This renders special relevance to our demonstration of magic numbers in mobility spectra, because it demonstrates, that in contrast to vacuum experiments, where the atomic clusters disappear in the mass spectrometer, we have them for further investigation behind the differential mobility analyzer (DMA). Thus, aerosol technology should open the possibility of doing chemistry on superatoms.

1.1. Principle of Operation

In the glowing wire generator, nanoparticles are produced by condensation from a supersaturated vapor. The material is evaporated by passing a high current through a conducting wire, suspended in a flowing inert gas. By mixing with the gas, the vapor is rapidly quenched. Assuming instantaneous quenching from melting temperature to 400K supersaturations in excess of $10^{10}$ are obtained for almost all suitable materials based on standard vapor pressure data [15]. Under these conditions rapid condensation occurs, forming nanoparticles.

The glowing wire generator is made mostly of standard stainless steel UHV parts. Figure 1.1 shows a schematic of the instrument. The wire is held in a 4 way cross by a current feedthrough with an embedded gas inlet. A water-cooled funnel forms the outlet on the opposite side to further cool the aerosol downstream. One of the remaining flanges is equipped with a viewport.

The wire is resistively heated close to its melting temperature by a DC low voltage/high current supply. The output remains most stable with respect to temperature and wire durability when operated under constant voltage, because the heating power reduces if the resistance of the wire increases according to

$$P_{\text{wire}} = \frac{U_{\text{wire}}^2}{R_{\text{wire}}}$$

(1.1)

With exception of tin and cadmium.
Chapter 1. The Glowing Wire Generator

Figure 1.1.: Schematic drawing of the glowing wire generator

Earlier attempts to stabilize the wire temperature via light emission used an infrared sensitive photocell \[16]. The photocell signal showed to be sensitive to the wire shape - which tends to change in the course of time - and fouling, which is hard to avoid. For this reason no feedback loop was applied.

In connection with studies on ion and electron emission from glowing wires, Langmuir \[17] proposed to control \(U_{\text{wire}}\sqrt{T_{\text{wire}}}\) in order to keep the temperature constant under consideration of wire diameter reduction due to evaporation. In this application the diameter only changes very slowly, which results in a change of some 10mA (< 0.1%) during the time of the experiments (hours). The constant voltage mode turned out to deliver a sufficiently constant aerosol output for the applications tested here.

The outlet funnel and the leads are water cooled to avoid desorption of surface contaminants inside the generator. The temperature of the aerosol directly behind the GWG has temperatures in the range around 90 – 120\(^\circ\)C for the materials investigated.

1.2. Material Considerations

In literature successful GWG-experiments are reported for the metals Ag, Fe, Be, Ni, Pt, Pd, W, Nb, Co and Zr. The fact that no particles were
1.2. Material Considerations

Ever detected from a gold wire is explainable by the lower vapor pressure of gold at the melting point compared to these metals. Evidently, there is a lower limit of the evaporation rate for particle formation to take place.

Based on the results of former experiments, a basic lower boundary for the amount of evaporated material is determined. This will give some indications on the suitability of metals for the GWG. Together with the results presented here it will give an idea of the expected resulting particle size distribution.

The wire evaporates at a rate \( r_m \) related to its vapor pressure \( P_s \) as described by the Hertz-Knutsen equation [18] if vacuum conditions are assumed:

\[
r_m = \lambda_{acc} \cdot \sqrt{\frac{1}{2\pi M_m N_a k_B T}} \cdot (P_s(T) - p_0),
\]

(1.2)

where \( \lambda_{acc} \) is the accommodation coefficient, \( N_a \) Avogadro’s number and \( M_m \) the molar mass. In the glowing wire generator the evaporated material is continuously transported away from the evaporation source and recondensation on the wire, related to the metal partial pressure in the surrounding atmosphere \( p_0 \), can be neglected. Some scattering of vapor molecules back to the wire surface by collision with the surrounding gas is accounted for by setting \( \lambda_{acc} < 1 \).

Thus \( \lambda_{acc} = 1 \) and \( p_0 = 0 \) represent an upper limit for the evaporation rate. The evaporation rate \( r_m \) determines the total particle volume produced per unit time, which is invariant in coagulation models as described by Lee et al. [19], Vermury and Pratsinis [20], Otto et al. [21] and others.

The material must coagulate to measurable particle sizes and concentrations in the time between generation and detection in order to be detected by aerosol measurement. The vapor density is the critical quantity determining the amount of detectable material. It critically depends on the evaporation rate, which is a material property and thus a crucial indicator for the suitability of a material.

Ordering the metallic elements by their evaporation rate at the melting temperature (see Table 1.1) leads to a list of usable materials. The experiments showed, that zirconium produced measureable nanoparticles, while gold did not, as several attempts in the past showed. The evaporation rate of Neodymium is close to Zr, and it was presumed it would produce
Chapter 1. The Glowing Wire Generator

detectable particles. The evaporation rate \( r_m \) rises monotonically with the vapor pressure \( P_s \) and thus an empirical rule for the applicability of the GWG leads to the condition

\[
P_s(T_m) > 5 \cdot 10^{-3} \text{Pa},
\]

where \( T_m \) is the melting point.

It must be noted, that the present set-up has a detection limit with respect to particle size, which is due to diffusion losses as well as the decreasing probability of carrying electric charge with decreasing size. The 2.5 nm particles in figure 1.5 (page 16) are hardly detected in the size distributions recorded. It is therefore plausible that materials with a vapor pressure lower or equal to gold still evaporate enough atoms close to their melting points to form small atomic clusters.

To extend the GWG to materials of lower melting point vapor pressures, coated wires can be used. Burtscher et al. [22] used a gold coated tungsten wire for particle production. This may be at the cost of purity, however, since not only the desired material is heated.

Complications regarding the production of pure particles also occur in connection with limited gas purity. Nickel wires oxidize, even when the highest available inert gas purities are used. This can be prevented by adding a few volume percent of hydrogen to the carrier gas. Other elements, e.g. tungsten and molybdenum, form oxides with vapor pressures close to the metal itself. This results in evenly strong evaporation of the oxide and the metal. Further, nitride formation occurs for some materials if heated in nitrogen atmosphere.

1.3. Measurement of Size Distributions

Size distributions and investigations on particle charging were carried out by electrical mobility analysis (see appendix A) with a home-made differential mobility analyzer (DMA, \( L_{DMA} = 114 \text{ mm}, \ r_e = 19.6 \text{ mm}, \ r_i = 9.35 \text{ mm} \)) followed by an aerosol electrometer (AEM). All flows were measured by rotameters. Sheath and excess air for the DMA where equaled by zeroing the difference with a bubble-type flowmeter. The inert gas flow was stabilized against pressure fluctuations. The DMA voltage and the electrometer output were set and taken by a LabView program through an
### 1.3. Measurement of Size Distributions

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<th>( r_m(T_m) ) [( \text{mol} \cdot \text{Pa}^{-1} )]</th>
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<th>( P_v(T_m) ) [Pa]</th>
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Table 1.1.: Metallic elements sorted by their evaporation rate (upper limit according to \( \lambda = 1 \) and \( P_v = 0 \) in eq. (1.2) at melting temperature \( T_m \). The saturation vapor pressure \( P_v \) is also shown. The elements indicated with a star have been successfully applied in the wire generator.
Chapter 1. The Glowing Wire Generator

Figure 1.2:
Setup for measuring particle mobility distributions of the total aerosol and the self-charged particles

A/D-adapter with 5 s delay between setting and reading. The aerosol flow rate was varied between 2 slpm and 4 slpm. While there is no principal restriction with respect to flow rate from the GWG, it was chosen not to increase the aerosol flow rate beyond 4 slpm with this type of DMA to keep the transfer function narrow enough ($Q_{sheath} = 17$ slpm). To obtain mobility distributions of the complete aerosol and the self-charged particles, the aerosol was directed through a three-way valve and fed either through a radioactive charger ($^{210}$Po $\approx 78$ MBq) or through a plain tube into the mobility analyzer (see Fig. 1.2). For comparison, the size distribution of the neutral particles was calculated from the mobility distribution obtained with the radioactive neutralizer, which applies the equilibrium bipolar charge distribution [23] as explained in appendix B.1.

For all tested materials the mobility distributions depend on the flow rate as can be seen in Fig. 1.4 for silver. In these experiments heat losses due to stronger cooling were compensated by increasing heating power in order to maintain the same color and thus evaporation rate of the glowing wire segment. Increasing the flow rate leads to a strong increase in numbers while the particle size decreases, which is expected from a simple coagulation model based on Brownian motion. At an initial stage monomers (atoms) collide with each other forming small clusters. As their number increases more and more cluster-cluster collisions take place, forming larger primary particles. Later these primary particles collide forming first aggregates and then agglomerates (see figure 1.3). The transition between formation of primary particles and aggregates is determined by
1.3. Measurement of Size Distributions

Figure 1.3.: Representation of a simple coagulation model based on Brownian motion. A supersaturated vapor initially grows by interatomic collision to small clusters, which then collide with increasing numbers to primary particles. At a later stage primary particles collide with each other and form aggregates and agglomerates, ultimately reaching a self-preserving log-normal size distribution.

basic material properties such as the melting point of the particles [24] and the surface condition, which under these conditions is mostly determined by adsorbate structure. Increasing the flow rate in the glowing wire generator reduces the transition time between the evaporation source and the measurement and thus coagulation time. Higher dilution further retards particle growth, because the collision rate is proportional to the square of the particle concentration.

Standard TEM grids (Cu with carbon film) where brought into the gas stream in a metallic filter holder to sample the particles for transmission electron microscope (TEM) analysis. The holder was placed inside the
Chapter 1. The Glowing Wire Generator

Figure 1.4:
Flow rate dependent mobility distributions with silver wire (⌀ 1mm) 99.9% purity using the neutralizer (a) and using the self charging effect (b). The same experiments were carried out using wire of 99.999% purity, measured with neutralizer (c) and using the self charging effect (d). In all cases positive particles were detected. The values in (a) and (c) are corrected for the charging efficiency of a radioactive charger.
1.3. Measurement of Size Distributions

branch parallel to the radioactive charger (see figure 1.2), so size distributions could be taken before and after the sampling without disturbing the generator.

Analysis (figure 1.5 for 2 slpm) essentially shows unagglomerated particles. For silver a size distribution with a mode around 2.5nm was observed. The primary particle mode is not reflected by the DMA spectra of figure 1.4, which is explained by the high diffusion losses for this size range. On the other hand, the high diffusion coefficient overrepresents these sizes on the micrographs. There is a strong convective circulation in the generator chamber, which was qualitatively observed in a separate experiment by blowing in smoke. Thus a fraction of the primary particles exit directly after formation and another fraction circulates one or more times, attaching further primary particles in the high concentration hot zone above the wire. High surface purity and elevated temperature lead to coalescence of the primary particles to form mostly round particles (see magnified area of figure 1.5) which represents an agglomeration mode observed in the DMA spectra. The bottom picture shows a palladium particle sampled under similar conditions but further away from the outlet of the GWG. Almost only agglomerates of primary particles with diameters of 2-3nm are visible. Due to the higher vapor pressure of palladium close to the melting point the vapor density is higher and more particles are formed. A combination of diffusion loss and high coagulation rate at higher particle concentrations leads to the distribution on the micrographs. Because of the high melting point of palladium, sintering is less complete as in the case of silver, producing partly sintered particles which still exhibit agglomerate shape.

Comparing figure 1.4(a) and (c) suggests that the particle size distribution is independent of the wire purity, considering that the reproducibility from measurement to measurement is limited.

Even for repeated measurements on the same wire, it was observed that the process of cooling and reheating induces changes in the crystal structure, changing conductivity. These slight changes have a significant effect on particle production through changes in the temperature profile of the wire and thus strongly influence the evaporation rate, which depends on temperature exponentially.

Palladium shows much larger particle sizes at similar process conditions (see figure 1.6(a) at 45.5W). This is due to the higher evaporation rate.
Figure 1.5:

top: Micrograph of silver nanoparticles from the wire generator (Ag, 99.99%, 0.8mm; N₂, 99.995%, 2 slpm). Sampled by diffusion, approx. 15min. The original size distribution is similar to the one shown in figure 1.4(a) and 1.4(c).

bottom: Micrograph of palladium nanoparticles sampled under similar conditions.
1.3. Measurement of Size Distributions

Figure 1.6:  
(a) Temperature dependent mobility distributions of Pd particles measured using a radioactive charger. The data is corrected for the charging efficiency, neglecting multiple charges. (Wire Ø 0.5mm, 99.95% purity, 1 slpm N$_2$, 99.995%)  
(b) Mobility distributions of self-charged particles from the same experiment. The mobility is expressed in terms of the mobility equivalent diameter of singly charged particles for better comparison with (a). The curves labelled (n) show the respective (uncorrected) data from (a). Solid lines are log-normal fits.
close to the melting point and thus more material is available in the particle formation zone. Palladium qualitatively shows the same behavior regarding the flow rate dependence as silver.

With palladium the effect of varying wire temperature was investigated. As can be seen from figure 1.6, the particle size decreases for lower temperatures. The reduction of particle size is explainable considering that with lower temperature the vapor concentration is reduced and thus less coagulation occurs, which leads to smaller modal diameter. Coagulation time is not significantly changed for low and high temperature and the higher particle concentrations suggests that the measurement at low temperature represents an earlier coagulation state.

At low temperature the particle size distribution has a geometric mean width of $\sigma_g = 1.4$ which is expected from a self preserving particle size distribution. For higher temperatures the mean width increases up to a value of $\sigma_g = 1.6$. Since the self preserving particle size distribution model is based on particles with no interaction forces it is expected that it does not hold for charged particles. The increasing fraction of charged particles of both polarities with increasing temperature changes the coagulation behaviour in favor of bipolar coagulation, resulting in increasing geometric mean deviations.

1.4. Particle Charging

The most straightforward explanation of electric charge emitted from heated surfaces is thermoemission of electrons. However, in the experiments on glowing wires both charge polarities were observed, while thermoemission only explains the negative polarity. Positive particles occur already at wire temperatures much lower than those predicted by electron or ion thermoemission theory. Elsewhere similar thermal charging effects are reported for aerosols [25, 26] and during thin film production from thermal sources [27–29].

Jeon et al. [29] heat silver in a tungsten basket and attribute positive ion formation to surface ionization of adsorbed silver atoms on an oxidized tungsten surface. In their model the data is only explainable if evaporation of ionized silver dimers and trimers is assumed. The experiments presented in this work with wires of different purities and with purifica-
1.4. Particle Charging

It is shown below that surface ionization of impurities explains the occurrence of positive particles, while negative particles are formed by thermoemission of electrons from the wire. A model is presented, which agrees with the measurements of charged particles presented here and shows that already small impurity concentrations are sufficient to explain the effect. This model also offers a more simple explanation to the data of Jeon et al. [28].

1.4.1. Theory

The phenomena of surface ionization and the emission of positive ions from heated metal surfaces are known since Richardson 100 years ago [31–33]. Adsorbed molecules/atoms charge more easily on a heated surface as compared to ionization in the vapor phase. The electron is transferred directly from the adsorbate to the substrate, and the activation energy of the process is defined by the difference between the ionization energy of the adsorbate and the work function of the substrate. The Saha-Langmuir equation [34, 35] describes the efficiency of positive charging:

\[
\alpha = \frac{n_+}{n_0} = \frac{g_i}{g_a} \cdot \exp \left( \frac{-e \cdot (U_i - \varphi)}{k_B \cdot T} \right)
\]

\[
\beta = \frac{n_0}{r_{subat}} = \frac{1}{1 + \frac{1}{\alpha}}
\]

Here \( \alpha \) represents the ionized fraction, \( n_+ \) and \( n_0 \) are the fluxes of charged and uncharged atoms of the same species evaporated from the surface, \( g_i \) and \( g_a \) are the thermodynamic sums of angular momentum states of the ion and atom, respectively. \( \varphi \) is the work function of the substrate and \( U_i \) the first ionization energy of the adsorbate. \( T \) represents the absolute temperature and \( e \) and \( k_B \) are the elementary charge and Boltzmann’s constant, respectively. \( \beta \) represents the charging efficiency in terms of the fraction of charged atoms with respect to the total evaporating flux of the adsorbate \( r_{subat} = n_+ + n_0 \).

Surface ionization theory predicts that many metallic materials show...
Chapter 1. The Glowing Wire Generator

<table>
<thead>
<tr>
<th></th>
<th>Ag (4.26)</th>
<th>Pd (5.12)</th>
<th>Ni (5.15)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$U_i - \varphi$</td>
<td>$\beta$</td>
<td>$U_i - \varphi$</td>
</tr>
<tr>
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<td>3.31</td>
<td>1.53 $\cdot 10^{-14}$</td>
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<tr>
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<tr>
<td>Ni</td>
<td>(7.63)</td>
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</tr>
<tr>
<td>Li</td>
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</tr>
<tr>
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<td>0.88</td>
<td>1.3 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>K</td>
<td>(4.34)</td>
<td>0.08</td>
<td>0.19</td>
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<tr>
<td>Mg</td>
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<td>3.88</td>
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</tr>
<tr>
<td>Ca</td>
<td>(6.11)</td>
<td>1.85</td>
<td>5.61 $\cdot 10^{-8}$</td>
</tr>
</tbody>
</table>

Table 1.2: Surface ionization energies ($U_i - \varphi$) and efficiencies $\beta$ for different combinations of substrates and adsorbates at the respective substrate melting temperature as calculated from equation (1.4). The numbers given in brackets give the work function ($\varphi$) and first level ionization energy ($U_i$) respectively.

For the frequently used materials silver, palladium and nickel the ionization probabilities are given in Table 1.2 for the metal and commonly found trace impurities. For the latter, namely the alkali and earth alkali elements, ionization efficiencies close to 100% are expected. A good review of surface ionization and the emission of positive charges is given by Zandberg and Ionov [38].

The total flux of positive particles is obtained by summing up all evaporated species weighed by their respective evaporation rates and charging efficiencies, since several components contribute to the positive current density:

$$J_+ (T) = e \cdot \sum_{i=1}^{n} r_i (T) \cdot \beta_i (T). \quad (1.5)$$

$\beta_i$ is the ionization probability of the $i$th component and $r_i (T)$ represents the total evaporation rate of the $i$th component per unit surface area. The evaporation rate of the bulk material is given by the Hertz-Knudsen equation. $N_a$ is Avogadro’s number and $r_m$ the molar evaporation rate as
1.4. Particle Charging

in equation equation (1.2):

\[ r_{\text{subot}} = N_a \cdot r_m. \]  

(1.6)

At high temperatures thermal emission of electrons can occur. The negative current density is calculated by the well-known Richardson equation with \( m_e \) being the electron mass and \( h \) being Plank’s constant:

\[ J_- = A \cdot T^2 \cdot e^{\frac{-\varphi}{k_B T}} \]  

with

\[ A = \frac{4\pi m_e k_B^2 e^2}{\hbar^3} \]  

in vacuum.

(1.7)

Assuming constant temperature over an infinitesimal small patch of wire surface the emitted net current density is given by:

\[ \frac{dI_{\text{total}}(T)}{dS} = (J_+(T) - J_-(T)). \]  

(1.8)

To obtain the emitted current of the total wire the contributions are integrated accounting for the temperature profile.

It is assumed that the evaporated material including ions completely condenses to form particles, thus the particles carry the entire charge emitted from the wire. \( I_{\text{total}} \) is then identical to the current measured by the aerosol electrometer apart from a factor accounting for particle loss to the walls. This assumption implies that particle growth is polarity-independent. Since loss depends on particle size, it becomes charge dependent if particles of different polarity grow differently. The charge dependence of particle loss can be neglected at the small electric fields present.

1.4.2. The Current of Charged Particles

The net current emitted by silver and palladium wires and carried to an AEM directly connected to the outlet of the GWG was measured. The

\[ \text{Silver: 0.8mm wire diameter, 99.99\% purity, palladium 0.5mm wire diameter, 99.95\% purity} \]
Net current emitted from a palladium wire measured by AEM directly connected to the outlet of the GWG. Measurements for increasing (up) and decreasing (down) temperatures are shown. The fit (solid line) with equation (1.11) yields $\Delta H_s = 2.77 \text{ eV}$ and $a_1 = 1.8 \cdot 10^{-6}$, with $U_i = 4.35 \text{ eV (K)}$, $\varphi_{subl} = 5.12 \text{ eV}$, C=18.02.

Results are shown in figure 1.7 for palladium and in figure 1.8 (see page 25) for silver.

For palladium (figure 1.7, left) the measurements recorded with increasing and decreasing temperature are in very good agreement with each other. The slight shift to the right for decreasing temperature is explainable by higher housing temperature, leading to less cooling at the wire ends and a slightly modified temperature distribution along the wire and, hence, the derived temperature is shifted.

The slight increase and plateau at low temperatures is expected to originate from volatile impurities with a low ionization threshold and high evaporation rate. The current due to these impurities decreases over time with decreasing surface coverage, which explains the smaller current at low temperatures when measuring downwards. This behavior is in good agreement with the measurements done by Wahlin, Barnes and others on ions from glowing wires in vacuum [33, 36].

Particles produced from a silver wire (figure 1.8) only show positive po-
1.4. Particle Charging

larity, because the temperature at the melting point is not high enough for significant thermoemission of electrons. The number of charges increases with increased wire temperature. Due to melting of the wire the measurements presented here stop at 1200K but measurements of Jeon et al. [29] can be understood as extension of the data beyond the melting point. They measured the ionic current from a heated Ag sample in vacuum using a tungsten basket for heating.

To validate the model using surface ionization and electron emission the wires are represented as 2-component systems. The substrate and a species of significantly smaller ionization energy are represented by molar fractions of \((1 - a_1)\) and \(a_1\), respectively. To obtain the evaporation rate of the i-th component, representing e.g. alkali metals (Li, Na and K) a generalized form of equation (1.6) is used:

\[
r_i = a_i \cdot r_{\text{subst}}.
\]  

(1.9)

The Clausius-Clapeyron relation is applied

\[
\ln P_s = -\frac{\Delta H_s}{k_B \cdot T} + C
\]  

(1.10)

to obtain the vapor pressure needed in equation (1.6), where \(\Delta H_s\) is the latent heat of evaporation\(^3\) and \(C\) a constant. Applying equation (1.8) and assuming a constant temperature profile over an "emitting" surface \(S\) of the wire one gets:

\[
\frac{I(T)}{S} = e \cdot \left( (1 - a_1) r_{\text{subst}}(T) \beta_{\text{subst}} + a_1 r_{\text{subst}}(T) \beta_1 \right) 
- \left( T^2 \cdot \exp \left( -\frac{\varphi_{\text{subst}}}{k_B T} \right) \right)
\]  

(1.11)

Inserting typical values of \(\beta\) (see table 1.2) and molar fractions \(a_1\) of impurities shows that the term representing the substrate material is neg-

\(^3\)Silver: \(C=17.76, \Delta H_s=2.96\text{eV}\), palladium: \(C=18.02, \Delta H_s=3.9\text{eV}\) from vapor pressure data [15].
Chapter 1. The Glowing Wire Generator

ligible, even for small values of $a_1$ and this term is dropped. Fitting was
done by using the least defined variables $a_1$ and $\Delta H_s$ as parameters. Equation (1.11) fitted to the high temperature region of the measured data is
shown in figures 1.7 and 1.8.

In case of palladium the general features are very well represented by
the model as shown in figure 1.7 on the right. The value $a_1$ of the ap-
parent impurity concentration is two orders of magnitude lower than the
amount of impurities in the material as specified by the manufacturer.
This indicates that only a small fraction of the impurities contributes to
the current. This is not surprising given the fact that not all impurities
have a low ionization threshold. Further the apparent impurity concentra-
tion contains inaccuracies introduced by the accommodation coefficient ($\lambda$
in equation (1.6)) and Richardsons’ constant ($A$ in equation (1.8)) which
cannot be separated. However, the values used for $\lambda$ and $A$ pose upper
limits, thus the obtained apparent impurity concentration has to be lower
than the specified value.

The apparent latent heat of sublimation $\Delta H_s$ is approximately 1eV
lower than the literature value for palladium (3.8eV, Lide [39]). This
value represents the binding energy of an impurity atom to the substrate
which is generally expected to be smaller than the binding energy of a
host atom. Further, equation (1.5) shows, that the latent heat of evapor-
ation and surface work function both enter this parameter and cannot be
separated. Variations in the surface work function $\Phi_{sub}$ due to experi-
mental conditions thus influence the prediction of latent heat, because the
fit assumes a constant value of $\Phi_{sub}$.

Although the general features of the measurements with palladium are
well reproduced by the model, large deviations are observed in the low and
high temperature limits. As already mentioned above, the current at low
temperatures is governed by volatile impurities. In the high temperature
region most likely recrystallization of the surface leads to an undefined
surface potential. At these temperatures also chemical reactions and ion-
ization of organic impurities from the gas phase can occur. In both cases
a two component model obviously oversimplifies reality and cannot repro-
duce the measurement completely.

In the case of silver the model predicts the temperature dependence
of generated charge in the aerosol (this work) and in vacuum [29] very
well over the whole temperature range. Due to the lower temperature
1.4. Particle Charging

Figure 1.8:
Net current emitted from a silver wire measured via the current of charged particles (this work) and via the current in vacuum (Jeon et al. [29]). The lines correspond to equation (1.11) with $\Delta H_s = 2.32$ eV and $a_1 = 4.6 \cdot 10^{-5}$ for the data of Jeon et al. and $\Delta H_s = 2.47$ eV and $a_1 = 3.2 \cdot 10^{-6}$ for this work. $\varphi_{subst} = 4.3$ eV (Ag), $U_i = 4.35$ eV (K). The data by Jeon et al. has been scaled by a constant factor.
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and work function of silver the system is much simpler with respect to contributing impurities (see table 1.2) and the two component model is a sufficient description.

In the aerosol measurement the value of $a_1$ is two orders of magnitude lower than the amount of impurities specified by the manufacturer. Under these conditions the emission of positive charge levels off at temperatures close to the melting point due to the onset of electronic emission. For the vacuum experiments the apparent impurity concentration is only one order of magnitude lower than specified, although the same material purities were used in both experiments. In this case an exponential increase over the whole temperature range is observed.

Besides different impurity compositions in materials from different suppliers, the higher purity in the presented case is explainable by the prolonged use of the wire, which leads to depletion of impurities over time. The method of Jeon et al. [29] requires a fresh piece of wire for every run and no outgassing was reported, thus the initial level of impurities is expected to be higher than in this case.

Representing the data for silver in an Arrhenius plot shows, that both vacuum and aerosol experiments agree very well over the whole temperature range in terms of activation energy. The values obtained for the apparent latent heat of sublimation are approximately 0.4eV lower than the literature values (2.85eV [39]).

1.4.3. Charging Efficiency

The mobility distribution of charged particles is shown together with the size distribution of the total aerosol in figure 1.9. The latter was obtained by establishing the equilibrium bipolar charge distribution on the particles by means of a bipolar aerosol charger [40] and correction with the known charging efficiency as function of size for a given polarity [41]. In case of the self-charged particles, no charge correction was applied. Both distributions can be fitted with log-normal functions. The self-charged and total aerosol distributions show large differences in mode size and width.

For the conditions given in the glowing wire generator coagulation can be assumed to be the only mechanism of particle growth [30]. Under these conditions a self preserving log-normal size distribution is predicted by theory [13] with $\sigma \approx 1.4$, which agrees well with the measured size...
1.4. Particle Charging

Figure 1.9:
Mobility distribution of self-charged (positive) particles and size distribution of the total silver aerosol. The same data as in figure 1.4 is used with a flow rate of 2slpm and wire purities of 99.9% (top) and 99.999% (bottom). The inset shows the log-log plot of the self-charging efficiency showing the volume dependence. $T \approx 1200$K
distribution of the total aerosol. Charged particles show a significantly broader distribution around $\sigma \approx 1.6$.

Tandem-DMA measurements showed very reproducibly, that the self-charged particles almost exclusively carry one charge in the size range investigated here. The ratio between charged and total aerosol concentration for a given size yields the size dependent charging efficiency. It was derived from data in figure 1.4 and plotted vs. particle diameter in a log/log-plot (figure 1.9 insets). The obtained graphs are straight lines with a slope close to 3, indicating that the charging efficiency is proportional to particle volume. This is expected if the charged species (ions or electrons) are present from the onset of coagulation. The growing particle then has a probability to be charged proportional to the number of atoms. This confirms the emission of ionized species from the wire and their presence during the particle formation process. If particle formation took place before ion attachment, the charging efficiency would be proportional to the particle diameter or surface (e.g. Hoppel and Frick [42]).

1.4.4. Charge Control by Wire Biasing

In the unipolar case of Ag, the charge is conserved during the growth process. In the bipolar case of Pd, it is symmetrical with respect to the polarities. Thus the charge distribution reached in the generator is not too far from the bipolar equilibrium distribution. The deviation of the self-charging mobility distributions in figure 1.6(a) from the cases involving the $Pd^{2+}$ neutralizer is systematic but small. Comparing of figures 1.6(b) and 1.6(a) shows that less than 10% of the Pd particles obtain a charge in the GWG at all settings of the power.

The concentration of self-charged particles can be increased by biasing the wire potential with respect to the surrounding metal housing. This may increase the charged particle yield by almost two orders of magnitude, as can be seen from figure 1.10(b). For particle sizes larger than 11nm, the self-charging efficiency at +60V bias is much larger than the efficiency of a radioactive bipolar charger. This was the largest bias the used current source allowed, whereas the trend suggests a further enhancement for larger bias voltages. The relative width of the size distribution shrinks from $\sigma \approx 1.5$ at low bias voltages to a value of $\sigma \approx 1.4$ at +60V bias, which is close to the value of the self-preserving log-normal particle
1.4. Particle Charging

Figure 1.10.:  
(a) Aerosol size distributions measured with radioactive charger at different bias and corrected for the charging efficiency of Boltzman equilibrium (Silver wire ® 1mm (99.9%) at 1lpm N₂ (99.995%)). (b) Mobility distribution of self-charged silver particles from the same experiment. The curve indicated with (n) is raw data taken with a radioactive charger for comparison. (c) Mobility distribution of positive self-charged particles from a palladium wire at different bias (Palladium wire ® 0.5mm (99.95%) at 1lpm N₂ (99.995%)) (d) Mobility distribution of negative self-charged particles from the same experiment.
size distribution [21, 43]. Biasing has only very little or no effect on the total aerosol as can be seen from figure 1.10(a). Evaporation rate and flow rate are maintained, so the external field alone is responsible for the enormous increase in charge. During the experiments on silver, no negative charge was detected. The increase in positive charge is thus not caused by removal of negative ions by attraction to the wire.

It is concluded, that positive ions emitted by the wire are more effectively drawn into the aerosol by the field. This is a well-known phenomenon on charge-emitting surfaces in air, documented for the first time by Hallwachs [44] in connection with the discovery of the photoelectric effect. Without the presence of an electric field, the emitted charged species diffuses back to the surface with a high probability, driven by the space-charge of the unipolar cloud and image charge forces. The enhancement of charged particles is partially compensated by the action of the field on the particles, drawing them to the wall. The growing loss of large particles, of which almost 100% are charged, with growing field strength is seen in figure 1.10(b). The loss of the small particles is overcompensated by the increase of charging efficiency.

Palladium (see figures 1.10(c) and 1.10(d)) shows much less influence of the external electric field on the concentration of charged particles. Here, electrons and positive ions are emitted simultaneously, space-charge effects are reduced and recombination is the major effect of mobile charge carrier loss. The external field separates the polarities, leading to enhancement for the polarity drawn away from the wire and loss for the polarity pushed towards the wire. Electrons are more mobile than positive ions, which explains the stronger effect on the negative polarity. The charged particle concentration is reduced/increased by a factor of two by biasing, much lower than in the unipolar case of silver. As pointed out before, the aerosol is more or less in Boltzmann equilibrium, since the mobility distribution does not differ significantly between external radioactive charging and self charging.

1.5. Conclusions

The origin of particle charge on nanoparticles produced from a heated wire [30] was investigated. Already at temperatures below the thermal
1.5. Conclusions

In the case of silver, only positive charge was measured. Temperature dependent measurements showed thermal activation with an apparent activation energy of \( \approx 2.3 \text{eV} \). A surface ionization model based on Saha-Langmuir, Hertz-Knutson, Clausius-Clapeyron and Richardson equations was used for description. It shows that trace impurities of potassium and other low ionization energy components present in any sample are sufficient to explain the charging behavior. The apparent latent heat of evaporation of this species on silver was found to be \( \approx 2.4 \text{eV} \), slightly lower than the latent heat of evaporation for silver (2.6eV). The deviation is explainable by a not well defined value for the surface work function of the substrate.

In case of palladium, positive and negative charge was measured. At low temperatures the net charge of the aerosol was positive and changes to negative at a temperature of approximately 1730K. This feature is reproduced by the model assuming potassium impurities on a palladium surface. The model correctly explains the change in net polarity, but other features in the current temperature dependence are not reproduced by the model. Obviously a two component system oversimplifies reality and different impurities and most likely changes in surface structure at high temperatures are responsible for the deviations.

The current of charged particles from a silver wire in a noble gas shows the same temperature dependence as the ionic current obtained in the vacuum experiment of Jeon et al. [29]. This shows that the surface of the wire is comparably clean with respect to adsorbates and that the use of a tungsten wire basket as evaporation source by Jeon et al. has no significant influence on particle charging. Their data was interpreted based on the model and found to be in very good agreement, providing a simpler explanation without the necessity of charged clusters. From aerosol size and mobility distributions the charging efficiency was derived as function of particle size. It is proportional to the volume of the particles, which implies that ions are already present at a very early stage of coagulation and do not significantly influence particle growth. This confirms that ions are emitted by the glowing wire and remain present in the vapor.

Biasing the wire leads to a strong increase in charged particle emission. In the unipolar case of silver the concentration of charged parti-
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Figure 1.11:
Flow scheme of nanocluster experiments. D=dryer, R=rotameter with valve, GWG=glowing wire generator, DMA=nano-DMA, AEM=aerosol electrometer, O=critical orifice, $Q_{\text{sheath}}$ = sheath air flow rate, $Q_{\text{excess}}$ = excess air flow rate, $Q_{\text{poy}}$ = polydisperse aerosol flow rate, $Q_{\text{mono}}$ = monodisperse aerosol flow rate.

icles is increased by almost two orders of magnitude, while in the bipolar, Boltzman-like case of palladium only a factor of two was observed. Charge carriers are more effectively drawn into the gas stream by an electric field \cite{44} which leads to the strong increase in charged particle concentration in the case of silver. For palladium recombination processes in the direct vicinity of the wire are dominant and reduce the effect of wire biasing.

1.6. Atomic Cluster Production

Mobility spectra of high mobility particles were taken using a nano-DMA similar to the type used by Rosell-Llompart et al. \cite{45}, with an inner radius $r_i$ of 4 mm, an outer radius $r_o$ of 9 mm, and a slit distance $L$ of 10 mm. It is equipped with a laminizer using a series of screens and special geometry to ensure laminar sheath gas flow. Figure 1.11 shows a scheme of the experimental setup.

Pressurized air is pre-treated with a silica gel dryer and a filter to remove any unwanted moisture and contaminants. The sheath air flow rate is set using a critical orifice and a pressure regulator. The excess air flow is
measured using a rotameter and passed through a HEPA filter. It is pumped at high sheath flows with a domestic vacuum cleaner to maintain atmospheric pressure in the DMA. Since the minimum excess flow rate is rather large due to restrictions of the pump, additional air is mixed to the excess flow through a three-way connection with an exchangeable outer orifice when operating at low flow rates. With this setup stable sheath flow rates up to $\approx 27 \text{ m}^3/\text{h}$ are obtained.

Sheath and excess air flows are matched adjusting the sheath air orifice backpressure and the power of the excess air pump. Flow balance is controlled by a bubble flow meter at the aerosol outlet with closed aerosol inlet. The aerosol inlet flow is typically set between 5 and 10% of the sheath air flow rate using a valve and rotameter. The monodisperse aerosol flow is actively drawn through an aerosol electrometer (AEM) for charge measurement using a dry rotary vane pump controlled by a rotameter.

Mobility measurements were performed by changing the potential between the central bullet and the outer core of the DMA between 0 and 5 kV using a high voltage power source controlled by an external signal. The voltage was either set through a computer via a digital/analog-converter or by scanning at very low frequency (3mHz) with a function generator using a triangular profile. Control voltage and particle concentration signal from the AEM are recorded through an analog/digital-converter. When scanning high voltage, the sweep rate must be slow enough to account for the physical response time of the DMA. Some lag is unavoidable, and mobilities recorded in an upward sweep are slightly different than those recorded in a downward sweep. The deviations are reproducible, and limited to a few percent. Long term measurements have shown excellent stability of flows and voltages, sufficiently long to perform a series of experiments.

The aerosol was analyzed directly from the source or after charging using external ion sources. Both a radioactive source ($^{210}$Po, $\approx 1.5 \text{ MBq}$) and a bipolar corona ionizer were used to produce gas ions, which charge the particles by ion attachment. The ionizer is placed in line between aerosol source and DMA.
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Figure 1.12:
Mobility spectra of air ions produced by a radioactive charger $^{210}$Po and a bipolar corona charger.

1.6.1. Results

Mobility spectra of particle-free air were measured with both types of ionizers. As seen from figure 1.12, four characteristic peaks at mobilities of $1.76 \cdot 10^{-4}$, $1.44 \cdot 10^{-4}$, $1.25 \cdot 10^{-4}$ and $1.02 \times 10^{-4}$ m$^2$/Vs are observed in both cases. When drying the air, the primary ion peak at $1.76 \cdot 10^{-4}$ m$^2$/Vs remains stable, whereas the other peaks decrease in relative height. We account these peaks to remaining water clusters. Different relative intensities of the peaks are either due to increased desorption or slightly varying preconditioning. Without an external ion source the measurement yields zero reading. Comparison between air and nitrogen yield no essential differences if the gases are sufficiently dried. Wiedensohler and Fissan [41] extrapolated mass and mobility of ions in air and nitrogen from aerosol charging data. Their values of $1.4 \times 10^{-4}$ m$^2$/Vs for air ions and $2.0 \times 10^{-4}$ m$^2$/Vs for ions in nitrogen are in reasonable agreement with the values obtained in our experiments. We believe that in nitrogen the ion spectra are dominated by impurities, since $N_2$ does not form ions. Thus it is not surprising that air and nitrogen give similar results. We ascribe the differences between the gases mainly to different water content.

In figure 1.13 mobility spectra from silver wires at different inert gas flow rates and wire temperatures are presented. Panel a) shows the the mobil-
1.6. Atomic Cluster Production

Figure 1.13.:
Mobility spectra of ions generated by glowing silver wires under different conditions. (a) aerosol flow rate $0.9 \text{ m}^3/\text{h}$ (15 lpm) with radioactive charger. (b) as before, but using the self charging effect. (c) mobility distribution for $0.3 \text{ m}^3/\text{h}$ (5lpm) aerosol flow rate using a radioactive neutralizer. The blank measurement shows the background ion spectrum under the same conditions. (d) mobility distribution of silver wire ions measured with a high resolution DMA (Hermann-type) calibrated with Tetra-Heptyl-Ammonium-Bromide. Data kindly provided by Prof. M.B. Attoui.
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ity distribution at 15 lpm taken with a radioactive neutralizer at different wire temperatures. The spectrum of water ion clusters is very pronounced at low heating power. With increasing wire temperature a broad feature emerges with a mobility less than $\approx 6 \times 10^{-5}$ m$^2$/Vs. Depending on wire temperature the maximum of this structure shifts. This broad feature exhibits the shape of a self-preserving log-normal size distribution\[13\], typical for aerosol produced by vapor condensation. The mode position is determined by vapor density, thus evaporation rate of the metal wire and dilution by the inert gas flow. When comparing the highest temperature mobility spectra for different flow rates we obtain good agreement with theory and previous experiments on larger particles\[30\]. At higher temperatures the prominent air ion peak at $1.76 \times 10^{-4}$ m$^2$/Vs decreases, which is expected to be due to collisional charge transfer from air ions to metal clusters, which indicates that there are metal clusters of higher stability in the positive charge state compared to the air ions.

In panel b) the aerosol mobility distribution measured without radioactive charger at the same aerosol flow rate is shown. The ions generated from the glowing wire show a comparable distribution as the ions generated by the radioactive neutralizer. The air ion peak ($\approx 1.76 \times 10^{-4}$ m$^2$/Vs) is less prominent in this case. New features occur at $\approx 7.5 \times 10^{-5}$ m$^2$/Vs and $\approx 1.2 \times 10^{-4}$ m$^2$/Vs. These features are believed to originate from small metallic clusters with magic numbers and are also observed at lower flow rates as shown in panel c) for 5 lpm aerosol flow rate.

Under these conditions the broad feature at small mobilities is more pronounced. This can be explained by the longer time it takes for the aerosol to travel to the DMA. Comparison with the blank ion spectrum of the radioactive charger an additional peak about $\approx 9 \times 10^{-5}$ m$^2$/Vs is visible.

Panel d) shows the data set of Attoui\[^3\] measured with a higher resolution DMA (Hermann type) without radioactive charger. The mobilities were calibrated with tetra-heptyl-ammonium-bromide (THABr) ions from an electrospray source, which explains the shift of the air ion spectrum with respect to the measurements shown in panel a-c. These spectra show a much more detailed peak structure, which changes with increasing heating

\[^3\]M.B. Attoui, private communication.
1.6. Atomic Cluster Production

Cluster physics has shown that there are preferred structures for certain geometric and electronic configurations called magic numbers. Geometric stabilization occurs for cuboctahedral and icosahedral shapes, whenever the number of atoms is sufficient to form closed surfaces [46, 47]. Giorgio and Urban observed three and fivefold symmetry in nanometer sized silver particles from a low pressure evaporation process [48, 49]. The symmetry is characteristic of geometrically stabilized clusters and the results agree with theoretical calculations [50].

An additional stability criterion is the completion of electronic shells as known from atoms. Especially in the case of silver, which has an electronic configuration comparable to alkali atoms, this effect was observed in vacuum cluster experiments [51]. In this case positive ions are investigated, which lack one electron, thus stability is predicted for 3,9,11 etc. atoms.

These geometric and electronic “magic number” clusters are also expected to be found in gas phase evaporation processes, but their small size and vicinity to gas ions obscures the spectra. Mobility spectra can be obtained from glowing wires without the use of additional chargers, thus the ions have to be generated by the wire itself. As shown in the previous section these ions can be impurity atoms or the metal itself. The volume dependence of the charging efficiency proves that charged clusters and particles of all sizes are expected. Based on that the temperature and flow dependent features of the mobility distributions are attributed to these small clusters.

According to Fernandez de la Mora et al. [11] the mobility for nanometer size particles is given by:

\[
Z = \frac{3q}{2P\delta_p^2} \left(\frac{kT}{2\pi m_g}\right)^{\frac{3}{2}} \left(1 + \frac{\pi \alpha_a}{8}\right),
\]

where \(q\) is the particle charge, \(P\), \(T\) and \(m_g\) are pressure, temperature and mass of the carrier gas, respectively. \(\alpha\) is the accommodation coefficient (0.911) and \(\delta_p\) is the collision distance. The latter is a combination of the particle diameter \(d_p\) and a correction term \(c\) via \(\delta_p = d_p + c\). \(c\) contains the collision diameter of the carrier gas molecules, \(\delta_g\), and other effects like physisorbed gas molecules. Based on mobility measurements of silver nanoparticles and proteins, Fernandez de la Mora et al. [11] determined \(c\)
### Table 1.3:
Overview of the identified peaks for silver. The diameter $d_p$ is based on the formula of Fernandez de la Mora et al. [11]. The number of atoms ($n$) is estimated using the bulk density ($10.5 \times 10^3 \text{kg/m}^3$). The last two columns give series of magic numbers for electronic and geometric stabilization [46, 47].

<table>
<thead>
<tr>
<th>$Z_{re}$ [10$^{-4}$ m$^2$/Vs]</th>
<th>$d_p$ [nm]</th>
<th>$n$</th>
<th>$n_t$</th>
<th>$d_t$ [nm]</th>
<th>$Z_t$ [10$^{-4}$ m$^2$/Vs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.445</td>
<td>0.65</td>
<td>8.5</td>
<td>3</td>
<td>0.46</td>
<td>2.058</td>
</tr>
<tr>
<td>1.220</td>
<td>0.76</td>
<td>13.3</td>
<td>9</td>
<td>0.66</td>
<td>1.416</td>
</tr>
<tr>
<td>1.220</td>
<td>0.76</td>
<td>13.3</td>
<td>13</td>
<td>0.75</td>
<td>1.231</td>
</tr>
<tr>
<td>0.930</td>
<td>0.94</td>
<td>25.8</td>
<td>21</td>
<td>0.88</td>
<td>1.014</td>
</tr>
<tr>
<td>0.930</td>
<td>0.94</td>
<td>25.8</td>
<td>35</td>
<td>1.04</td>
<td>0.814</td>
</tr>
<tr>
<td>0.790</td>
<td>1.07</td>
<td>37.5</td>
<td>41</td>
<td>1.10</td>
<td>0.759</td>
</tr>
<tr>
<td>0.770</td>
<td>1.09</td>
<td>39.7</td>
<td>55</td>
<td>1.21</td>
<td>0.664</td>
</tr>
<tr>
<td>0.710</td>
<td>1.16</td>
<td>47.5</td>
<td>59</td>
<td>1.24</td>
<td>0.642</td>
</tr>
<tr>
<td>0.710</td>
<td>1.16</td>
<td>47.5</td>
<td>93</td>
<td>1.45</td>
<td>0.517</td>
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<tr>
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<tr>
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<td>561</td>
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<tr>
<td>923</td>
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<td>0.152</td>
<td>923</td>
<td>3.11</td>
<td>0.152</td>
</tr>
<tr>
<td>1415</td>
<td>3.59</td>
<td>0.119</td>
<td>1415</td>
<td>3.59</td>
<td>0.119</td>
</tr>
</tbody>
</table>
to be 0.53nm for air. Applied to the measurement data in figure 1.13 panel a-c the particle sizes listed in table 1.3 are obtained. Based on the bulk density of silver the number of atoms in the cluster is estimated and compared to the values of the magic number series for electronic and geometric stabilization [46, 47]. Within experimental error, we obtain agreement of our measurement with these values, considering that several parameters in the calculation as bulk density, collision diameters and adsorption layers on the clusters are unknown or badly defined at this scale and conditions.

Applied to the data of Attoui (figure 1.13 panel d) values do not agree as good, because the spectrum is shifted. Direct intercomparison of these values however is difficult, because the plotted data work with different aerosol/sheath air ratios and thus must still be normalized with the width of the transfer function, which is not available to the author. This typically introduces a shift in peak position, which is not accounted for in the given representation.

A final proof of the existence and the separation of atomic clusters by mobility analysis can only be given by mass spectrometry.

1.6.2. Conclusions

The mobility of air ions produced by radioactive radiation and bipolar corona discharge was measured. Four characteristic peaks at mobilities of $1.76 \times 10^{-4}$, $1.44 \times 10^{-4}$, $1.25 \times 10^{-4}$ and $1.02 \times 10^{-4}$ m$^2$/Vs were found. The primary peak at the highest mobility is attributed to ionized gas molecules, whereas the others belong to water clusters. The mobilities agree well with values expected from aerosol charging [52] for air and nitrogen. When the gas was sufficiently dried, no significant difference in the mobility spectra of nitrogen and air was found.

Investigations of the mobility spectrum of silver nanoparticles produced by a glowing wire with electric mobilities larger than $10^{-5}$ m$^2$/Vs showed structures besides the expected broad coagulation mode at mobilities larger than $10^{-4}$ m$^2$/Vs. Comparisons with magic numbers show agreement for geometrically and electronically closed shells [46, 47, 51]. However, the peak structure and calculated values for “magic number series” cannot be conclusively matched to the measurement data without mass spectrometer analysis. Comparison with calibrated mobility data from Attoui shows a systematic shift, which originates from different normal-
Chapter 1. The Glowing Wire Generator

ization of the data and complicates matching of peaks.

A combination of mobility classification and mass spectrometry is necessary to finally confirm the existence of small metallic “magic” clusters in the aerosol spectrum.
1.7. Summary

The glowing wire method forms a very useful tool to produce nanometer sized particles of a large variety of materials. The primary particle size can go down to the domain of atomic clusters. A minimum vapor pressure of \( P_s(T_m) = 5 \times 10^{-3} \text{Pa} \) was defined for the wire material in order to form particles detectable by standard aerosol equipment. With high end nano-DMA technology, however, particles containing only some atoms are detectable, which links cluster physics and aerosol technology.

Depending on the conditions these primary particles coagulate and coalesce forming larger structures with size distributions close to log-normal. Depending on the melting point and process conditions, unagglomerated round particles as well as aggregates and agglomerates of round particles are formed. The primary particle diameter and aggregate or agglomerate structure depend on sintering behavior, which is determined by size dependent melting point, surface mobility of the atoms and surface purity. For very small particles the melting point is high and surface mobility low. As two of these particles collide complete sintering is likely. For larger particles surface mobility and melting point are lower and incomplete sintering is expected. This suggests that a lower size limit for aggregates/agglomerates exists.

Since only the desired particle material is heated, particles produced from a glowing wire are pure with wire purity as the determining factor. Mean size and concentration are controllable via flow rate, temperature and bias voltage.

The large portion of self-charged particles allows the production of highly concentrated, nearly monodisperse aerosols by mobility classification. Particle concentrations up to \( 10^6 \text{ cm}^{-3} \) are obtained with a standard DMA with a relative mobility bandwidth around 0.1. Radioactive chargers are redundant, which avoids safety precautions. Polarity and charging efficiency are closely related to purity and operating temperature of the wire and are exponentially dependent on time [38].

Self-charging can be explained by combining surface-charging and thermal emission of electrons. For materials with low melting point the glowing wire produces only positive particles, whereas at higher wire temperatures also electrons are produced by thermal emission. Positive charge is typically carried by ionized alkali impurities in the wire material and
already present in the vapor before coagulation. The self charging efficiency is dependent on the number of atoms in the particle and scales with the $3^{rd}$ power of the diameter. In the unipolar case of silver we observed no significant influence of charge on particle growth. We assume, however, that in case of palladium bipolar coagulation is enhanced due to the presence of both polarities in the aerosol phase. The width of the particle mobility distribution depends on wire temperature and thus on charge levels.

The fact that small clusters can be produced by the glowing wire method and subsequently separated in differential mobility analyzers enables the study and application of chemical reactions involving atomic clusters for the first time. Numerical calculations and low pressure experiments indicate [14], that small metallic clusters have an atom-like behavior. Aerosol technology is well suited to produce new types of materials and material structures for chemistry and catalysis.
Chapter 2.

Particle Morphology
Classification

“But I don’t want to go among mad people,” Alice remarked. “Oh, you can’t help that,” said the Cat: “we’re all mad here. I’m mad. You’re mad.”
“How do you know I’m mad?” said Alice. “You must be,” said the Cat, “or you wouldn’t have come here.”

(Carroll [5])

Nanostructured materials are especially interesting for surface based processes as e.g. catalysis or membranes because of their very high surface area as compared to their volume and thus weight. It is evident that the surface structure also plays an important role in surface processes [53]. Nanoparticles and clusters grown in the gas phase often show a large variety of geometric forms [54], called morphologies or crystal habits. They often differ from the lowest free surface energy structure, which is called Wulff polyhedron. Due to rapid quenching and large influence of interatomic interactions, so called growth structures, form on the size
Chapter 2. Particle Morphology Classification

scale of atoms and clusters based on different growth rates of individual crystal faces. In the size range from 1nm to 5nm a large variety of atomic clusters with exceptionally stable geometric and electronic configurations at so called magic numbers was observed in the past [e.g. 48–50, 55, and others].

Although size effects are investigated on a large scale, morphology dependences are not widely recognized and investigated. This is largely due to a lack of suitable equipment for classification and separation. Previously a separation stage for particle morphologies was designed and tested based on the photoemission properties of nanoparticles [4]. In this study nanoparticles of different materials were separated and the results reproduced by numerical modeling. Round silver primary particles and dimers of these with identical surface area were separated.

An analytical mathematical model was derived to predict the behavior of the instrument and verified with experimental and literature data. A numerical solution was calculated for comparison with previous work [4] and to obtain design parameters for improvement. Experiments where performed to test different instrument configurations.

2.1. Principle of Operation

Monodisperse nanoparticles are exposed to ultraviolet radiation and negative gas ions simultaneously, while deflected in an electric field inside a modified differential mobility analyzer. The electric mobility \( Z_p \) of the particles depends on their charge, which is determined by two competing processes: photoemission and ion attachment (Appendix B). The rate of photoemission reflected in the photovield is accessed if the particle undergoes a number of charging/decharging\(^1\).

UV-radiation causes the emission of electrons, thus charging the particles, while the attachment of negative ions discharges the particle. The emission rate of photoelectrons depends on photon flux and particle properties (charge, material and surface state; see eq. (B.14)). The attachment

\(^1\)Here “charging” describes the process of making a particle “more positive”, thus a particle with charge \( q = -1 \) is in a higher charge state than a particle with \( q = -2 \). Accordingly, discharging is the transition into a lower charge state (\( q \to q - 1 \)).
2.2. Experiment and Results

rate of negative ions only depends on the ion concentration and particle charge (see eq. (B.4)), if a monodisperse aerosol is used. It is insufficient to use photoemission only for separation because the obtained maximum charge does not depend on morphology sensitively enough. On the other hand the photoelectric yield at a given wavelength close to the photothreshold strongly depends on the material and the surface state\(^2\). The state of the surface is different for different morphologies, because it depends on the orientation of the crystal faces present at the surface.

The separation stage measures the electric mobility \(Z_p\), which changes proportional to the charge of the particle. It fluctuates while passing through the irradiated region and only particles which have traveled with proper average radial velocity/electrical mobility can exit the separation stage, very similar to the traditional DMA (appendix A). The monodispersity of the initial aerosol allows to separate the constant particle properties from the fluctuating charge, thus finally the time averaged mean charge \(\overline{q}_t\) determines, which particles exit the separation stage (fig. 2.1, right). It is given by

\[
\overline{q}_t = \frac{1}{\tau} \sum_{i=0} q(t) \Delta t_i \tag{2.1}
\]

\[
\tau = \sum_i \Delta t_i.
\]

2.2. Experiment and Results

The separation stage (fig. 2.1) is realized by replacing the outer electrode of a standard cylindrical DMA by a quartz glass tube. A fine metal mesh inside the glass tube acts as transparent outer electrode for the instrument \[4\]. It is connected to the metallic parts by a gold grid electrode evaporated directly on the glass surface. The glass differential mobility analyzer (GDMA) is placed in a wooden box with 4 low pressure mercury lamps

\(^2\)Surface state is used to describe the crystal surface structure and the adsorbant state together.
Chapter 2. Particle Morphology Classification

Figure 2.1:
Schematic of the separation stage. On the right a random particle trajectory is shown composed from paths of different slope depending on the charge state of the particle.

(Philips TUV mini, TUV8WFAM) producing about 2.1W UV-C radiation each, at a wavelength of 253.7nm. The emission lines with higher energies are filtered out by the glass tube of the lamps, while the visible light has insufficient energy for photoionization. Therefore only one wavelength contributes to photoemission.

The transmission of the glass is close to 98% at 254nm wavelength (Suprasil, Heraeus). The gold grid and metal mesh on the outer electrode have 54% and 30% open area, respectively, which results in a total open electrode area of 16.2%. Transmission of glass and metal together are \( \approx 15.9\% \), thus the transmission coefficient becomes \( \kappa_{GD} = 0.159 \).

For all separation experiments a silver aerosol was produced from the glowing wire at 1 slpm nitrogen with 99.995% purity (chapter 1). In a first experiment an open system as shown in figure 2.2 (top) was used. The aerosol was size selected by a first DMA (FDMA) operated with 10 slpm sheath air and 0.3slpm where extracted into the GDMA, which was operated with 3slpm sheath-air. The particles were detected at the monodisperse outlet by a condensation particle counter (CPC, TSI UCPC 3025A). The excess aerosol was filtered and discarded.

With this setup a shift of the mobility distribution towards higher mean charge was observed, but no separation of particles with respect to morphology was observed. The use of air as sheath gas introduced impurities
2.2. Experiment and Results

Figure 2.2: Flow diagram for morphology separation experiments. Open setup (top) and closed loop setup (bottom). PR = pressure reducer, GWG = glowing wire generator, GDMA = glass DMA

which uncontrollably modify the photoemission properties of the particles. As the adsorbate situation is not identical for each particle this increases the width of the charge distribution and the morphology influence on photoemission is covered by the effect of adsorbates. Burtscher et al. [22] have already reported that the bulk surface work function of silver could only be measured if ultra-pure helium from the liquid phase was used. Even purification in a liquid nitrogen cold trap proved insufficient.

To increase purity in the separation process, the DMA sheath air system was changed from open- to closed-loop systems as shown in figure 2.2 at the bottom. Flushing the closed-loop system with nitrogen removed
Figure 2.3: Mobility distribution of silver particles measured with the GDMA in a closed loop setup with and without radiation (left). For comparison the results of Kirsch [4] scaled to the same process conditions as in these experiments are shown (right). The sampling voltages for figures 2.4 and 2.5 are shown by dotted lines, respectively.

any residual air and allowed to work in a pure nitrogen environment. A slight overpressure upstream of the DMA additionally prevented intrusion of air. Figure 2.3 shows a typical mobility distribution in terms of the deflection voltage. Evidently, the influence of impurities on the particle work function was reduced sufficiently to reveal two peaks representing different morphologies (see below).

The residence time in the GDMA is $\approx 5s$ at typical flow rates used in this study (2.3slpm), while adsorbate monolayers are already formed within $\approx 1s$ at impurity levels in the ppb range. These levels are usually only achievable with baked out high purity systems. Adsorbed impurity molecules must be present, but the difference in the photoelectric yields of the two morphologies is still significant enough to allow separation. In other words, the high sensitivity of the photoyield with respect to gas adsorption demonstrated by Burtscher et al. [22] must not hinder the separation of morphologies.
2.2. Experiment and Results

To identify different particle types the aerosol was sampled electrophoretically at different voltages of the GDMA for offline analysis. Micrographs of particles collected from the experiment shown in figure 2.3 at 22V and 34V, i.e. the two modes, are shown in figure 2.4.

Only slight differences in particle shape are observed. The micrographs show that particles sampled at lower voltage are composites of two particles of roughly the same size, while particles sampled at higher voltage are either unagglomerated or show only one much smaller particle attached to it. To ensure negative ion transport, the center electrode of the GDMA is kept on negative potential with respect to the outer cylinder. At the same time, this voltage attracts the positive particles to the center rod. A lower deflection voltage thus corresponds to a higher electric particle mobility or a higher mean charge state.

The particles sampled at 22V GDMA voltage (\(\bar{\eta} = 1.64e\)) thus emit photoelectrons more frequently than particles sampled at 34V (\(\bar{\eta} = 1.06e\)). The particles initially have the same mobility and thus the same surface area but exhibit different photoelectric behavior. Similar results were obtained earlier by Kirsch [4] on the same instrument, but with particles produced in a tube furnace. In these experiments the separation stage was operated at approximately four times higher flow rates (10 slpm), which reduces the residence time to about 1s. Scaling the respective data to the same process conditions as in the present experiments, the results agree very well (see figure 2.3). The particles in the experiment by Kirsch showed more pronounced differences in morphology, as seen in figure 2.3.

The results can be explained qualitatively by the effect of enhanced photoemission for small particles as reported by Schmidt-Ott et al. [8]. This implies that aggregates behave much like the primary particles they are composed of with respect to photoemission. The photoyield (equation (B.11)) depends strongly on the electric interaction between the particle and the emitted electron, which must overcome the Coulomb barrier between electron and particle. The electron induces an image charge below the surface as it is drifting away. This potential depends on surface curvature and thus particle radius [56]. Obviously, the surface curvature of agglomerates is closer to the properties of primary particles than of solid particles, which suggests to use the primary particle diameter for calculation of the effective work function (eqn. (B.12)) for agglomerates, rather than the agglomerate diameter.
Figure 2.4:
TEM micrographs of silver nanoparticles collected at $q_t = 1.64$ (top, 22V GDMA) and at $q_t = 1.06$ (bottom, 34V GDMA) in a closed loop setup. [Ag-wire, $\varnothing$ 1mm 3N, $U_{bias}$ 60V, FDMA at 120V (16nm)]
2.2. Experiment and Results

Figure 2.5.: Micrographs by Kirsch of particles separated by photoemission at $\bar{q}_t = 1.66$ (bottom) and at $\bar{q}_t = 1.04$ (top) in the GDMA (with kind permission).
In traditional photoemission theory it is required that electrons excited inside a particle have a wave vector perpendicular to the surface larger than the surface potential in order to escape. Faraci et al. [57] suggest that this only applies to large particles. In case of very small particles the surface has much more steps and irregularities and more angles of incidence are perpendicular to the surface which implies that the enhancement as reported by Schmidt-Ott et al. [8] depends on the surface structure. This is an effect determined by primary particles rather than the agglomerate as a whole.

Both the geometrical escape probability effect and the image charge effect should be observable for small particles within an agglomerate, while they are probably weakened by electronic contact. Kirsch [4] suggests that oxide layers may inhibit electronic contact. However, oxide layers on this size scale are merely tunneling barriers which reduce electron transport rather than completely inhibiting it and cannot lead to significant electronic insulation between particles. Oxidic layers between particles of this size are further expected to be inhomogeneous and would contain a lot of "holes" for electrons to pass.

To support the hypothesis that the size-effects in photoemission are basically retained in an aggregate of small particles, the system was examined analytically based on semi-empirical assumptions, which are presented in the following section.

2.3. Analytical Description

Mathematically, the charging dynamics in the irradiated region of the GDMA can be reduced to a Markov-chain problem, which is a system of differential equations describing the time evolution of the population density in any given state. Neighboring states are coupled through transition rates. If the system has a limited number of states an analytic solution can be found for constant transition rates.

In case of the separation stage the lowest charge state $q_{\text{min}}$ is determined by attachment of negative ions (table B.1) and the highest charge state $q_{\text{max}}$ is defined by the effective work function (equation (B.12)). The resulting equation system (2.3) contains $C_M \cdot (q_{\text{max}} - q_{\text{min}} + 1)$ differential equations describing the time evolution of the populations in different
2.3. Analytical Description

charge states $N_q$, $C_M$ represents the number of species distinguished by their photoemission properties (surface state and material). Each equation contains source and sink terms which account for particles entering and leaving a charge state by photocharging and diffusion decharging. All equations are coupled by the ion concentration $n_{ion}$ contained in the ion attachment rate (equation (B.4)). If the ion concentration is constant the electron emission and ion attachment rate become constant and only neighboring states are coupled. In this case the system reduces to a Markov-chain problem, which is very similar to bipolar charging, and the solution can be transferred.

\[
\frac{dn_{ion}}{dt} = \sum_{C_M} \sum_{q=q_{min}}^{q_{max}} \rho_{pe}^{q-(q+1)} N_q C_M \]

\[
\sum_{C_M} \sum_{q=q_{min}}^{q_{max}} \rho_{ia}^{q-(q-1)} N_q C_M \]

\[
\frac{dN_q C_M}{dt} = \rho_{pe}^{(q-1)-q} N_q C_M - \rho_{pe}^{q-(q+1)} N_q C_M \]

\[
+ \left( \rho_{ia}^{(q+1)-q} N_q C_M - \rho_{ia}^{q-(q-1)} N_q C_M \right) \]

The time evolution of the concentration of positive and negative ions is accounted for by two additional differential equations. In case of the separation stage no positive ions are present and equation (2.2) is sufficient to define the system. Ions are produced by photoemission, while ion attachment to particles depletes them. Strictly speaking the equation should contain additional source and sink terms for ions emitted by the center electrode\(^3\) and lost to the walls. However, in this case steady state conditions for the ion flux to and from the electrodes are assumed and these terms cancel. When additionally the concentration of ions gener-

\(^3\)The center electrode emits electrons, which get quickly captured by the surrounding gas molecules forming ions.
Chapter 2. Particle Morphology Classification

ated by the center electrode can be assumed to be much higher than the concentration produced by the particles, \( \frac{dn_{\text{ion}}}{dt} \) becomes zero and the equation can be dropped completely, leaving the Markov-chain.

The probability \( \psi_{q,C}^{\beta CM} \) of the particle to be in a certain charge state then is calculated according to equation (2.7). Because the system is limited by minimum and maximum charge states, the steady state charge distribution is an estimate for the distribution of time averaged mean charges of a single particle after a large amount of events. The same is true for mean charges, thus \( \tilde{q}_t \) obtained from the steady state charge distribution is an estimate of \( \bar{q}_t \) for large \( t \):

\[
\tilde{q}_t = \sum_q q \cdot \psi_{q,C}^{\beta CM} \quad \text{at} \quad t \rightarrow \infty \quad \tilde{q}_t
\]  

(2.4)

The charging/decharging rates \( \rho \) entering system (2.3) contain particle dependent properties \( \eta \) and instrument dependent properties \( J_{\text{Photon}} \) and \( n_i \):

\[
\begin{align*}
\rho_{\text{pe}}^{q \rightarrow (q+1)} &= \eta_{\text{pe}}^{q \rightarrow (q+1)} J_{\text{Photon}}(\nu) \\
\rho_{\text{ia}}^{q \rightarrow (q-1)} &= \eta_{\text{ia}}^{q \rightarrow (q-1)} n_i^{-}
\end{align*}
\]

The photon flux density \( J_{\text{Photon}} \) can be estimated for a lamp positioned at a distance \( r_{L/DMA} \) away from the center of the separation stage (see figure 2.6). Via the spectral energy of the lamp \( P_{\text{Lamp}} \) the number of photons is calculated, which evenly distribute over a cylinder with radius \( r_{L/DMA} \) and length \( L_{\text{Lamp}} \).

\[
J_{\text{Photon}} = \frac{P_{\text{Lamp}} \kappa_{\text{GD}}(\nu)}{2 \pi r_{L/DMA} L_{\text{Lamp}} h \nu} \quad (2.5)
\]

The light passes the quartz glass and the electrodes (figure 2.1), which determine the transmission coefficient \( \kappa_{\text{GD}} \). Based on the dimensions of the experimental setup\(^5\) and the lamp characteristics the photon flux den-

---

\(^4\)Definition see appendix B

\(^5\)\( P_{\text{Lamp}} = 2.1W, r_{L/DMA} = 0.1m, L_{\text{Lamp}} = 0.25m, h \cdot \nu = 4.88eV \) (254nm), \( \kappa_{\text{GD}} = 0.159 \) (see page 46). [4]
2.3. Analytical Description

Figure 2.6:  
Left: Measures determining $J_{ce}$ (not to scale)  
Right: Regions illuminated with 2 (dark gray), 3 (gray) and 4 (light gray) lamps. The white circle in the middle represents the center electrode (scale).

The ion concentration $n_i$ can be estimated from the photon flux density, when assuming that ions are generated mainly by photoemission from the
center electrode, which is true if the ion concentration is not affected by particle charging. Steady state conditions require the same ion flux through the inner and outer electrodes of the GDMA. Ions are fed into the separation volume at a constant rate and accumulate until the first ions leave the separation stage after crossing the separation volume. Thus the number of ions generated during the ion lifetime $\tau_{ion}$ (eqn. (A.2)) and distributed evenly through the separation volume yields an approximation for the steady state ion concentration according to

$$n_{ion} = \frac{J_{Photon} Y_{ce} A_{ce} \tau_{ion}}{V_{sep}} = \frac{J_{Photon} Y_{ce} r_{i} \ln \left( \frac{r_{a}}{r_{i}} \right)}{2 Z_{ion} U_{DMA}}.$$  \hspace{1cm} (2.6)

Along the radial direction the ion concentration varies slightly because the flux of ions from the center electrode is constant, but the volume in which they are contained increases with $r^{-1}$. The ion concentration on the last 10% of the particle trajectory is approximately twice as high as compared to the first 10%.

The photoyield of the center electrode is $Y_{ce} = 8.34 \cdot 10^{-6}$, based on a bulk work function of $\varphi = 4.5$ eV for stainless steel and an estimated emission constant of $K_{c} = 4 \cdot 10^{-4}$ eV$^{-2}$. D’Arcy and Surplice [58] report that the work function of stainless steel varies slightly, when the surface is on electric potential. These studies, however, were performed under vacuum conditions and it is assumed that the effect of adsorbate layers is much more predominant and field effects are neglected. Figure 2.6 shows that the center electrode is irradiated by two lamps at almost any position and the photon flux for ion emission from the electrode is based on the radiation intensity of two lamps. It becomes

$$n_{ion} = 7.03 \cdot 10^{14} \text{ ion} / \text{m}^{3}.$$  \hspace{1cm} (2.6)

Typical particle concentrations downstream of a mobility selection stage are in the range of $10^{11} - 10^{12}$ m$^{-3}$. Because the GDMA is operated at low

$^{6}$\text{Z}_{ion} = 2.15 \cdot 10^{-4} \frac{\text{m}^2}{\text{V}}$, Wiedensohler and Fissan [41]
2.3. Analytical Description

Flow rates, the voltages $U_{DMA}$ are in the order of tens of volts. Under these conditions the influence on the ion concentration from particles will be one to two orders of magnitude smaller than the background ion concentration, which justifies dropping equation (2.2).

The particle dependent properties for photoemission as described in appendix B.2 are based on classical photoemission theory. They include size dependent modifications of the work function, which lead to decreased photoactivity. Measurements by Schmidt-Ott et al. [8], Müller et al. [59, 60] have shown that the photoemission constant $K_c$ also varies with particle size. Müller et al. [60] report that the emission constant for 3.8nm diameter particles is enhanced by a factor of 255 as compared to the bulk value in high purity measurements, while Schmidt-Ott et al. [8] report enhancement factors between 20 and 120 for particle sizes between 4nm and 6nm. It is assumed that the factor of 2 between these measurements is due to impurities on the surface of the particles which change the reflectivity of the particle boundary (compare B.2). To reflect this enhancement effect in the present calculations an exponential increase of $K_c$ with decreasing particle size is assumed according to:

$$285 \cdot \exp \left( - \frac{r_p}{8 \cdot 10^{-9}} \right).$$

This allows for a gradual decay of the photoemission constant from a value of approximately 250 at 1nm radius to a value of less than 10 at 15nm radius. This function is used for convenience and not based on a specific theory and thus a rough estimation. In order to obtain more specific information on the nature of this effect high purity, high accuracy measurements on different materials (metallic and non-metallic) and particle sizes are necessary, which are beyond the scope of this thesis. Emission factors of a material with $\varphi = 4.4$ eV are shown in table B.3 for different particle radii together with the respective enhancement coefficient. Particle dependent contributions for negative ion attachment are calculated as described in appendix B.1.

In the previous section it was shown, that the GDMA separates two different particle morphologies in an silver aerosol: round particles and aggregates of smaller primary particles. While the photoemission proper-

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7see equation (B.11)
Chapter 2. Particle Morphology Classification

Figure 2.7:
Photoemission coefficient $\eta pe^q \to (q+1)\eta pe^q$ for round particles (left) and aggregates with 10nm primary particle diameter (right) including enhancement.

Photoemission properties of spheres are well defined as described in appendix B, assumptions must be made for the photoemission properties of aggregates, to simulate their behavior in the separation stage. It is expected that electron emission is dominated by the surface properties of the primary particles, while light and already emitted electrons interact with the aggregate.

In this approach aggregates are simulated with the photoyield $Y$ enhanced according to the primary particle diameter, while the Coulomb interaction of the emitted electron with the particle is based on the aggregate, i.e. that electrons are emitted from a primary particle, but "see" the aggregate when diffusing away. The photosensitive surface area and the absorption probability are based on the aggregate as well. For the size range under investigation it can be assumed that the mobility is surface proportional. This means that the photoactive surface area of a sphere with the same mobility is equal to the agglomerates surface area.

Figure 2.7 shows the positive emission constants for solid, round particles and aggregates composed of primary particles with 10nm diameter. For round particles a characteristic bump in activity due to enhancement at small sizes is observed. For larger round particles enhancement and surface curvature are negligible and the emission factors approach bulk
2.3. Analytical Description

values. Aggregates do not show a local maximum since the enhancement factor is fixed by the primary particle size. The emission coefficient simply depends on the active surface area and the adsorption probability and thus scales with \( r_p^3 \) until the adsorption probability reaches 1 and then continues proportional to \( r_p^2 \) for larger particles. In terms of absolute values, emission factors of agglomerates are higher than those of round particles by the enhancement factor of the primary particles - about one order of magnitude at 10nm primary particle diameter.

Based on the photoemission constants for round particles and aggregates charge state probabilities \( \psi^{a,C_M} \) are calculated recursively from differential equation system (2.3) and shown in figure 2.8. As expected from the photoemission constants aggregates charge to higher charge states than round particles. For the latter the local maximum in the emission coefficient is also reflected in the charge distribution.

The differential equation system only yields charging probabilities for multiples of the elementary charge, thus the charge state probabilities for an individual particle at steady state. For particles passing the separation stage the values shown at fractional charge can be interpreted as a first order approximation for the probability to obtain a certain time averaged mean charge \( \bar{q}_t \) at large \( t \). For a large number of particles the charge distribution is an estimate for the charge distribution measured at the outlet of the GDMA, from which it is possible to determine the width of the measured mobility distribution and the resolution of the separation stage.

The separation stage is operated with negative potential on the center electrode to sustain a continuous negative ion flow from the center to the outer electrode. Accordingly only particles with positive time averaged mean charge \( \bar{q}_t \) can be detected. Figure 2.9 shows the time averaged mean charge calculated from the results of equation system (2.3) through equation (2.4).

At high ion concentrations (\( 10^{15} \text{m}^{-3} \)) negative mean charge is predicted for solid, round particles (left panel) for diameters smaller than 30nm. Aggregates with 5nm diameter primary particles (right panel) are predicted to be negative when smaller than 20nm. At lower ion concentrations almost all particles obtain positive mean charge. As shown experimentally in the section above (figure 2.3) aggregates of 20nm mobility equivalent diameter obtained a time averaged mean charge of 1.65e, while solid, round
Figure 2.8:
Calculated charge state distribution of a material with $\varphi_\infty = 4.4\text{eV}$ obtained in the separation stage for round particles (top) and aggregates of 5nm (middle) and 10nm (bottom) primary particle diameter ($n_{\text{ion}} = 7.03 \cdot 10^{12}/U_{\text{DMA}}, J_{\text{photon}} = 8.16 \cdot 10^{18}$).
2.3. Analytical Description

Figure 2.9:
Time averaged mean charge $\bar{q}_t$ in the separation stage for solid particles (left) and agglomerates of primary particles with 5nm diameter (right) dependent on the ion concentration (in m$^{-3}$). $h\nu = 4.86\text{eV}$ (255nm), $\varphi = 4.4\text{eV}$, $J_{\text{Photon}} = 8.16 \cdot 10^{18}$.

particles of the same diameter obtained 1.05e. These charge levels are analytically predicted at ion concentrations between $10^{13}$ m$^{-3}$ and $10^{14}$ m$^{-3}$.

To rate the performance of the separation stage the difference $\Delta \bar{q}_t$ between the time averaged mean charge of aggregates and round particles of the same diameter is calculated and shown in figure 2.10. It is an approximation for the relative distance of the peaks, since the electric mobility is directly proportional to voltage. Aggregates with 5nm primary particle diameter (left) are separated better from round particles than aggregates consisting of primary particles with 10nm diameter (right). In the latter case the enhancement factor is smaller than in case of 5nm particles and the difference between the photoemission rates is smaller. The absolute values of the differences in the time averaged mean charge are comparable to the values obtained experimentally for 20nm diameter aggregates of 10nm diameter primary particles and round particles (see previous section).

The width of the size distribution is not considered in this analytic model and no final conclusion on the resolution can be drawn. The ion concentration in the separation stage varies with the voltage between the
Figure 2.10.: Difference of mean charge ($\bar{q}_t(solid) - \bar{q}_t(agg)$) between solid particles and agglomerates with 5nm (left) and 10nm (right) primary particle diameter, for different ion concentrations (in $m^{-3}$).

Electrodes (equation (2.6)) and the ion attachment rates depend on this parameter (equation (B.14)), which has direct effect on the mean charge. Particles with different photoemission properties thus experience different ion concentrations, which is not reflected in equation system (2.3). To include it, the particle charge must be calculated iteratively. An easier way to consider this effect is to use Monte-Carlo methods for the simulation of the charging dynamics and to simultaneously solve the equations of motion for the particles in an electric field.

2.4. Numerical Description

As explained in the previous section the analytical solution requires steady state conditions and the background ion concentration is the same for all particle types. In reality this is not true, because the ion concentration depends on the voltage at which a particle is extracted from the separation stage, e.g. a particle with higher time averaged mean charge experiences a higher background ion concentration because it is extracted at lower GDMA voltage. This again has direct effect on the mean charge, because
2.4. Numerical Description

the ion attachment rate depends on the background ion concentration. At lower ion concentration it takes statistically more time for ions to decharge a particle and the time averaged mean charge increases. This requires a lower extraction voltage in the GDMA thus the particles experience a higher ion concentration decreasing the mean charge. To correctly estimate the voltage at which particles with certain photoemission properties leave the separation stage must thus be obtained iteratively from the analytic model. For the same reason the analytic model only gives limited information on the width of the measured mobility distribution and a performance rating of the resolution is difficult based on this information.

Computational simulation, which uses Monte-Carlo methods to simulate the charging behavior while simultaneously solving the equations of motion for the particles, was performed to include the effect in the model. A similar approach was successfully applied to separation of two different materials by Kirsch [4], but the variations in ion concentration with the applied GDMA voltage were neglected.

The charging dynamics of photoemission and ion attachment was also calculated by Maisels et al. [61] including the changes in ion concentration by particle charging, but this model did not solve the equations of motion for the particles in an electric field. The present approach simulates charging dynamics in the separation stage under the assumption that the negative ion concentration is not influenced by particle charging and determined completely by the GDMA voltage. For the particles the same assumptions as in the previous section were made, i.e. round particles behave "normally" with respect to photoemission, while aggregates show an enhanced photoyield corresponding to their primary particle size. The Coulomb interaction of the agglomerate remains the same as for "solid" particles. Figure 2.11 shows a flow diagram of the computer program.

The transition rates are transferred into probabilities for the Monte-Carlo approach by multiplication with a time step, which yields the number of charging events (per time step). If this number is smaller than unity it can be understood as a charging probability, which can be applied to a single particle. To determine whether a particle changes its charge state, a random number\(^8\) between 0 and 1 is added to the probability. If the

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\(^8\)This program uses the random number generator class "Mersenne Twister" by Wagner [62], which is based on an algorithm by Matsumoto and Nishimura [63].
Chapter 2. Particle Morphology Classification

Figure 2.11.: Flow diagram of the simulation program.
2.4. Numerical Description

result is larger than 1 the particle changes its charge state, otherwise it remains unchanged. This is done for each particle in each time step for ion attachment and photoemission.

After calculation of charge, the particle is moved in radial direction along a linearized electric field and it is checked if it hits the inner or outer electrode. In this case the particle is marked as exited and not considered for further charging or motion. If the particle hits the inner electrode at the position of the exit slit, it is counted for the mobility distribution. The particles are charged and moved until the transition time through the separation stage (defined by sheath and aerosol flow rates) is reached. Then the electric field is increased and the calculation starts again, to calculate the complete mobility spectrum.

External parameters of the separation stage like dimensions, light intensity, initial ion concentration, ion mass etc. can be set at will. Particle properties like primary particle diameter, emission constant and bulk work function are easily changeable. To save computation time, the ion attachment coefficients are calculated separately according to equation (B.3) and hard-coded into the program for charge states between -15 and 15. Changing the agglomerate diameter thus requires recompilation of the program and so do changes of the scanned GDMA voltage range. The simulation time depends on the number of simulated particles, time step and number of charging/decharging events and range from several minutes to a few days for the systems investigated in this work.

For the simulation particles with the properties compared to silver are used\(^9\) and the dimensions of the separation stage are chosen as described in the previous section. Figure 2.12 shows the results of simulations with different ion concentrations for agglomerates with primary particles of 5nm and 10nm diameter. The calculated time average mean charge of the particles agrees very well with the values obtained from the analytical solution under the same conditions.

Aggregates consisting of primary particles with 5nm diameter separate from round particles of the same mobility equivalent diameter at all investigated ion concentrations. With increasing ion concentration the distance between the peaks corresponding to the two particle species also increases. The same trend is found for aggregates consisting of primary

\(^{9}\)The detailed parameters for the simulation are listed in appendix F.
Figure 2.12: Simulated mobility spectra of a mixture of round particles and aggregates with 5nm (top) and 10nm primary particle diameter (bottom). The simulation is based on silver particles with an mobility equivalent diameter of 22 nm and a flow rate of 2.3 slpm in the GDMA. The conditions are comparable to section 2.2. Particle size and material also agree with the experiments by Kirsch [4].
2.5. Conclusion

In this chapter the properties of a morphology separation stage were discussed theoretically and experimentally. An analytical model was derived to describe the behavior of metallic nanoparticles under irradiation of ultraviolet light in an atmosphere containing negative ions.

The experiments performed earlier by Kirsch [4] were repeated in a similar manner under different process conditions. The results agreed

particles with 10nm diameter, but at the lowest investigated ion concentration ($10^{12} \text{ m}^{-3}$) the two particle species are not separated, opposing to the predictions from the analytic model. This is accounted to the missing coupling between the ion concentration and the DMA voltage as explained above. At ion concentrations around $10^{13} \text{ m}^{-3}$ a peak structure comparable to the experimentally measured values is observed, but the time averaged mean charge is higher than in the experiment.

The material properties entered in the analytic and numeric model are usually measured under controlled, clean conditions, i.e. vacuum or high purity gas environment. The conditions in the separation stage are much less controlled and deviations, especially for the electron work functions $\varphi_{\infty}$, are expected. This has influence on the photoemission of the particles and the background ion concentration, which depends on electrons emitted from the center electrode. These parameters both strongly influence the time averaged mean charge and the separation between the particles, but a combination to exactly resemble the experimental results has to be found by trial and error.

Although the assumptions regarding the photoemission properties of aggregates and solid, round particles in the model are yielding qualitatively good results, the correctness cannot be quantitatively determined from the model due to the large number of factors influencing the photoemission process, e.g. the composition of impurities in the separation stage is expected to influence the work function. Nevertheless, the model indicates that particle separation by morphology is possible based on a few, basic assumptions and that qualitative results in the same order of magnitude as observed in the experiment are obtained for a set of physically reasonable parameters.
qualitatively and quantitatively, but TEM analysis of the particles showed small variations in shape in the present case, which can be ascribed to the production method.

The problem was accessed analytically by solving the master equation for the particle charge states under the assumption of constant coefficients. It was shown that particles with different photoemission properties obtain different time averaged charges and thus show different effective electric mobilities. The calculations were based on a mixture of agglomerates and round particles with the same mobility equivalent diameter and primary particle diameters of 5nm and 10nm. To explain the differences in photoemission, aggregates were assumed to have the photoyield of the primary particles and the effective surface area and radiation absorption properties of the aggregate. The size dependence of the photoyield was extended by an exponential enhancement factor, which was fitted to the data of Müller et al. [60]. The results indicated that aggregates and round particles of equal mobility can be separated in the GDMA. The ion concentrations at which mobility spectra matching the experimentally obtained shape qualitatively are found, are ten to 100 times smaller than estimated from initial instrument specifications. However, these estimations are based on the electronic work function of the clean material, which is expected to be lower than in the less pure conditions of the current experiments. A higher work function of the center electrode would lead to much lower electron emission and consequently lower ion concentrations.

The analytical solution was unable to reproduce proper separation of the particle species. A Monte-Carlo simulation was used to incorporate the effects of coupling between photoelectric charging (increasing the mobility) and the negative ion concentration, which is increased via the GDMA voltage for increased mobility. This simulation can be brought to agreement with the experimental findings, using realistic particle properties with respect to photoemission.

The separation stage was experimentally proven to separate aggregated particles from round ones. The results confirmed that the GDMA can be used for morphology separation of nanoparticles. It was shown that a certain degree of purity is necessary to guarantee separation, but adsorbate-free ultra-clean conditions are not necessary. It is unclear whether the difference in photoelectric behavior leading to separation can be regarded as a size effect of the pure primary particles in the aggregate or an effect
2.5. Conclusion

of the surface under the influence of gas adsorbates.
Chapter 3.
Catalysis on Nanoparticles

Among the possible applications of gas phase production and classification of nanoparticles by the methods treated in the present thesis, catalysis is certainly a very important one. This chapter shows an example of the usefulness of these methods for basic investigations in heterogeneous catalysis.

Due to quantization effects nanoscale materials differ strongly from bulk with respect to mechanical, chemical and optical properties. Electronic structure and surface morphology are two of the major factors influencing materials on this scale. It is obvious that processes taking place at or on the surface are thus strongly influenced by particle size and surface conditions. Strong size effects are observed as e.g. the activation of nanoscale
gold for the oxidation reaction of CO [65] or soot oxidation by platinum clusters [66, 67].

While size effects have already been discussed for a long time, there are myriad effects of a size-modified electronic structure, that have not been systematically investigated, yet. Previous work usually studied the adsorption behavior or binding strength of molecules and molecular ions [68–71], or the influence of catalyst support [72–75]. The latter is often known as strong metal support interaction (SMSI) and accounted to changes in the electronic structure. Only few studies relate charging effects directly to catalytic properties [76–79].

The influence of an electric field on the catalytic behavior of alumina supported platinum catalyst was investigated for the oxidation of hydrogen and of silica supported palladium catalyst for the hydrogenation of ethene. These experiments were performed in microreactors. For the oxidation of hydrogen a small dependence on the electric field was found, while the hydrogenation of ethene seems to be independent of the electric field strength. In a different set of experiments the activation energy of unsupported nickel catalyst for the methanation reaction of carbon monoxide was measured depending on particle charge. These experiments showed significant dependence on charge.

### 3.1. Supported Catalyst

It was experimentally shown by the present study that charge induced by an electric field into supported nanoparticles has an effect on catalytic activity in case of the oxidation of hydrogen. Microreactors are cost efficient and require only small quantities of catalyst, which can be easily produced and classified in the gas phase. In combination with mass spectrometry they form a quick and useful system for fast catalyst screening. The design applied is limited to gas phase reactions. Impedance spectroscopy was successfully applied for catalyst characterization.

#### 3.1.1. Reactor Design

The microreactors for investigation of the oxidation of hydrogen in this study were made from two parts. Standard silicon wafers coated on one
3.1. Supported Catalyst

Figure 3.1:
Side view of the initial micro-reactor design. a) Upper and lower part of the reactor. b) & c) Connection and sealing.

side with an aluminium film were used. The particles were supported on the native oxide on these films. As shown in figure 3.1 two strips of $1.5\,\mu\text{m}$ thick mylar foil were used as spacers between the upper and lower reactor parts. The foil formed the side walls of the reactor channel. The aluminium films were electrically connected with gold coated contacts. The two parts were sandwiched between two glass plates for additional strength and finally sealed with adhesive resin. To avoid electric short circuiting between the two electrodes the particle-free aluminium layer was covered with spin coated PMMA\textsuperscript{1} (not shown in figure 3.1).

The reaction channel acted as critical flow obstruction determining the flow rate into the vacuum system containing a quadrupole mass spec-

\textsuperscript{1}Polymethylene-methacrylate (Plexiglas)
Chapter 3. Catalysis on Nanoparticles

Figure 3.2.: Side view of the final micro-reactor design.

trometer. Although comfortable to use, the flow pattern and speed change throughout the channel inducing changing reaction conditions. For the experiments on the hydrogenation of ethene, the reactor concept was slightly altered, as shown in figure 3.2.

The mylar foil is replaced by 1.3 \( \mu \)m thick photoresist typically used in semiconductor processes with an etched micro-channel. The catalyst is supported by the native oxide of the silicon wafer, while the aluminium electrode is on the outside of the reactor, not on the inside as before. A tempering step after aluminium sputtering ensured good electric connection between the two materials. The reactor components were glued with a removable resin, which allowed the study of the catalyst structure by atomic force microscopy (AFM) before and after use.

While in the first experiments the reactor channel itself formed a critical orifice, limiting the flow through the reactor towards vacuum, the new design has the critical flow obstruction at the end. This ensures a longer residence time in the catalyst containing region due to a lower face velocity and a steady flow regime over the whole length of the channel.

The microreactor plate was fixed in a vacuum flange (figure 3.3) for connection to the vacuum system and the mass spectrometer. The high-pressure side of the reactor is situated in a chamber at ambient pressure, continuously flushed with the reactant gases.
3.1. Supported Catalyst

Figure 3.3.: Reactor holder.

3.1.2. Catalyst Characterization by Impedance Spectroscopy

To electronically characterize the catalyst particles, impedance spectroscopy was used. The top and bottom sides of the microreactor are connected to the electrodes of a network analyzer, measuring the response of the system to AC-excitation ($30 - 3 \cdot 10^6$ Hz frequency, $50 \text{mV}$ peak-to-peak amplitude). The AC-voltage is additionally biased by a DC voltage (-1.5 - 2.5 V). Figure 3.4 (top) shows the equivalent circuit for a particle loaded reactor.

The particles are supported by an insulating aluminium or silicon oxide layer. At oxide thicknesses of only a few nanometers, electrons can tunnel through the barrier if empty electronic states are available in the particle. The electronic states, i.e. conduction and valance state bands, can be shifted by an external electric field. As the Fermi-level (FL) of the particle is below the FL of the substrate (silicon) electrons tunnel into the particle and other way around for the opposite polarity, as shown in figure 3.4 (bottom). The energy dissipated by the current is measured by the network analyzer and the dielectric function is calculated. From these values resistances and capacitances of the system are recovered. Based
Figure 3.4:
Equivalent circuit for impedance spectroscopy (top) and electronic structure of the biased particle substrate system (bottom).
3.1. Supported Catalyst

Figure 3.5:
Repeated impedance spectroscopy measurements on Pt particle loaded reactors (Pt/Al₂O₃ system). Parallel lines in one plot are taken at different frequencies, with the lowest frequency giving the highest capacitance. The measurements shown in the last plot were taken after a rest period of several days.

on the response at different frequencies, the characteristic timescale for tunneling can be determined.

Particle-loaded reactors showed characteristic structures in impedance spectroscopy experiments, which were not observed in particle-free reactors. An example is shown in figure 3.5 (top left), where parallel lines represent measurements at different frequencies. Low frequencies result in high capacitances, high frequencies in low capacitances. This can be understood when the tunneling behavior is considered. The tunneling process has a characteristic timescale and as long as the characteristic timescale of the electric field (AC-component) is longer as the tunnel-
Repeated impedance spectroscopy measurements on Pd particle loaded reactors (Pd/SiO$_2$ system). The measurements were taken after a rest period of 2 days (left) and 3 days (right).

In a second set of experiments palladium catalyst particles supported by native silica was used. Figure 3.6 shows two impedance spectroscopy measurements with the second one recorded after several days. No deteri-
oration of the signal is observed, which implies that no anodization occurs. Nevertheless, the measured structure changes over the course of days due to rearrangements of the particles. If particle surface bonding is weak enough to allow (limited) particle motion on the surface at room temperature, it takes several days for the particles to reach a stable position on the surface. This process is well known from semiconductor and thin film technology, where atoms rearrange and typically find their lowest energy state at surface defects. After stabilization, the reactor is used for chemical reactions and further restructuring is induced by reaction enthalpy. In principle, this allows the study of catalyst modification by rather simple means and in-situ, without the need of microscopic techniques.

The results of impedance spectroscopy are linked to the band structure of the nanoparticles \cite{81, 82} and e.g. the band-gap of semiconducting particles can be measured. Norskov et al. \cite{83} states a relationship between the adsorption energy and catalytic activity for some dissociative reactions. In chemisorption the binding energy of a molecule to the surface also depends on the availability of electronic states in the substrate material which can bond to the molecular orbitals. Thus screening nanoscale catalyst materials by impedance spectroscopy can be a tool to predict catalytic behavior.

### 3.1.3. Oxidation of Hydrogen

In a first study the electronic structure of a platinum catalyst was changed by an electric field and the influence on the oxidation of hydrogen was investigated. Standard silicon wavers from semiconductor processes coated with sputtered aluminium were used. The silicon acted as ultra flat support, while the aluminium was used as an electrode. The catalyst particles were deposited by diffusion and supported by the native aluminium oxide layer on one side of the reactor, while the other one remained particle-free.

From AFM measurements it is known that Pt particles used for the oxidation of hydrogen are probably smaller than a few nanometers. They were only detectable as increase in surface roughness on the silicon wavers. Only few large particles with height around 5nm were observed, while the majority of the particles was in the height range around 1nm. Height was used as measurement criterion, because the horizontal resolution of the AFM is limited due to convolution with the shape of the probe.
Chapter 3. Catalysis on Nanoparticles

The model reaction is easy to perform and takes place already at ambient temperature. Therefore complicated heating mechanisms were avoided in the first test. Based on UHV studies the reaction is considered to occur as a three step Langmuir-Hinshelwood mechanism [84, 85]:

\[
\begin{align*}
O_{ad} + H_{ad} & \rightarrow OH_{ad} \quad (3.1) \\
OH_{ad} + H_{ad} & \rightarrow H_2O_{ad} \quad (3.2) \\
O_{ad} + 2H_2O_{ad} & \rightarrow 3OH_{ad} + H_{ad} \quad (3.3)
\end{align*}
\]

The latter route includes an autocatalytic step, which is only expected to play a role at ambient pressure, where the amount of surface adsorbed water is significant. The dissociation of oxygen and hydrogen is generally considered to be the catalyzed step. Then the rate limiting reaction step is (3.1) in UHV-experiments, whereas at ambient pressure the autocatalytic step (3.3) is believed to be rate limiting.

Due to high background concentration of the product the measurements performed on this reaction only allow qualitative conclusions. Figure 3.7 shows the catalytic activity of the particle-loaded reactor at different bias voltages before and after aging. In the top left figure the dependence of the bias voltage on catalytic activity for a new reactor is shown. Positive and negative bias both increase the rate of water formation, a positive bias stronger than the negative bias. After aging the reactor for 22 days the total catalytic activity with no bias has increased by approximately 5 times as compared to fresh reactor material (bottom left). However, no significant influence of the electric field can be observed any more (right figures).

It is assumed, that the catalyst is initially not in equilibrium state with respect to the substrate and that catalyst particles can move rather freely on the surface. The chemical reaction and the electric field additionally transfer energy that increases surface mobility. The rearrangement of catalyst particles to the lowest energy state leads to the increase in catalytic activity after aging, probably due to strong metal support interaction (SMSI) on the alumina support. The decrease in sensitivity with respect to the electric field is expected to originate from a change in particle-surface interaction and possibly partial oxidation of the catalyst material.
3.1. Supported Catalyst

Figure 3.7:
Bias dependent measurements on Pt loaded microreactor for different bias voltages and exposure times. Top left: Activity of fresh catalyst material for different bias voltages. Bottom left: Activity of catalyst material after 1, 2 and 22 days resting time without bias. Right: Activity of Pt catalyst after 22 days resting time dependent on bias.
Chapter 3. Catalysis on Nanoparticles

The blank reactor initially showed similar behavior with respect to bias voltage as the particle loaded reactor. Even under exclusion of oxygen, water was detected. A possible explanation is field induced desorption of water, another one is formation of water by reduction of the aluminium oxide layer. The latter Mars-van-Krevelen mechanism was proposed by Hendriksen and Frenken [86–88] for oxidation reactions of CO.

Because of the large background and the difficulties to avoid water contamination of the reactor together with undefined desorption behavior of water under the influence of an electric field the possible conclusions are very limited. Indications that charged particles have a strongly modified catalytic behavior are seen but doubts arise because the blank material shows similar results. For this reason more experiments were performed with a different reaction and the improved microreactor design.

3.1.4. Hydrogenation of Ethene

To avoid difficulties in product detection, undefined reaction paths and high background levels, the hydrogenation of ethene was chosen as a model reaction. This has the major advantage that the product ethane does not naturally occur in the environment and that the reaction only takes place at elevated temperatures. All detected ethane must originate from the catalytic process. Temperature control allows determination of the activation energy from an Arrhenius-plot. Variations in the activation energy can then be attributed to different charge states of the catalyst. Silica is generally known to be inert as support material and thus all chemical reactions are expected to take place at metallic catalyst sites. The reactor according to the improved design described in section 3.1.1 is applied. Altogether this system is expected to be more defined and to give better results than the previous setup.

\[
\begin{align*}
C_2H_4 + \uparrow & \leftrightarrow C_2H_4^\dagger \quad (3.4) \\
H_2 + 2\uparrow & \leftrightarrow 2 H^\dagger \quad (3.5) \\
C_2H_4^\dagger + H^\dagger & \leftrightarrow C + 2H_2 + \uparrow \quad (3.6) \\
C_2H_6 + H^\dagger & \leftrightarrow C_2H_6 + 2\uparrow \quad (3.7)
\end{align*}
\]
Figure 3.8:
Arrhenius plot of the hydrogenation reaction of ethene in the temperature range from 30-90°C. The concentration is corrected for the temperature dependence of the velocity in the reactor.

The reaction mechanism follows the Horiuti-Polanyi route [89], which is supported by density functional theory (DFT) calculations by Hansen and Neurock [90]. Ethene is chemisorbed on the palladium surface and reacts stepwise with coadsorbed dissociated hydrogen. The chemisorption of ethene involves electron exchange of \( \pi \)-electrons from the double bond with the substrate [90]. Similar to the chemisorption of CO on nickel (see page 92) the C-C bond strength is expected to depend on the charge state of the catalyst particles.

A series of measurements dependent on temperature and bias was performed to obtain an Arrhenius-plot as shown in figure 3.8. No significant dependence of the activation energy on the electric field in the microreactor was found. However, the activation energy determined from this plot is in the range of 10kJ/mol, about 3 times lower than the literature value of 30kJ/mol [91, 92].

An increase in total ethane concentration was observed with increasing electric field at all temperatures. From the Arrhenius plot it is concluded that the activation energy of the reaction is unchanged. The increase in total concentration must then be due to an increased reactant concentration.
or a higher throughput through the reactor. Since the feed composition is unchanged throughout the experiments, the channel dimensions must have changed with the electric field. The forces exerted by the electric field are believed to have widened the channel and increased the flow. A widening of the channel also results in a decrease of the electric field and thus hinders field dependent measurements. At present adsorption/desorption effects on the reactor walls cannot be excluded, which lead to steadily increasing ethane concentrations.

3.1.5. Conclusions

The Activation energy of the hydrogenation of ethene on $\text{Pd/SiO}_2$ catalyst was measured in a microreactor with respect to an electric field applied to the reactor walls in the temperature range from 303-363K. The activation energy was determined to be 10kJ/mol, three times lower than the literature value of 30kJ/mol [91, 92]. No significant changes of the apparent activation energy with changing electric field were found, but an increase in total ethane concentration dependent on the applied voltage was measured. However, this might be due to changes in channel width induced by electric forces leading to increased throughput. Furthermore desorption from the walls might influence the overall product concentration.

At the present stage the influence of electric fields on the catalytic activity in this specific case cannot be excluded, especially since the support material influences Pd catalysts for the hydrogenation reaction of ethene. It is known that electron interchange with the catalyst takes place during chemisorption [90] which is expected to be influenced by electric charge on the particles. A more careful analysis of the reaction order and the reaction conditions should help to clarify this topic.

3.2. Unsupported Catalyst

The lack of conclusiveness of the preceding experiments is mainly due to effects of the substrate and walls. An experiment avoiding these effects was therefore designed.
3.2. Unsupported Catalyst

3.2.1. Introduction

In catalysis strong metal support interaction (SMSI) is long known to influence the activity of catalyst materials. While certain substrates are inert as e.g. silica, others such as titania are known to enhance the catalytic activity of refractory metals. Due to the inhomogeneous nature of catalyst supports it is difficult to separate electronic and morphological effects. Recent studies\cite{78, 93} indicate that SMSI can be explained by charge exchange between catalyst and substrate.

Aerosol methods give access to the particle surface without the need of a substrate. If well-defined particle production is possible, this should enable controlled basic studies on catalysis. Single reaction steps can then be identified more easily by controlled modification of the material. Seipenbusch\cite{94} and Weber et al.\cite{95} have investigated the catalytic activity of unsupported nickel catalyst in the methanation reaction of CO and found turnover rates up to 100 times higher than for comparable supported catalyst systems.

CO bond strength can be directly related to the infrared vibrational stretching frequency and studies on carbon monoxide adsorbed on transition metal surfaces are widely available\cite{96–99}. Zhou et al.\cite{100} investigated the CO stretching frequency of metal carbonyl molecules and ions in noble gas matrices and found a red shift with increasing electron density. Frank et al.\cite{76} measured the linear stretching frequency of CO adsorbed on small Pd, Rh and In clusters supported on alumina substrate. Comparison with Zhou et al. yielded different charge transfer for clusters situated on flat surfaces ($\pm 0.2e$) as for those located at line defects ($+0.5e$). Hoffmann et al.\cite{93} prepared Pt catalyst on titania activated silica substrates. Depending on the preparation method different amounts of titanium were incorporated into the silica surface, which influenced the oxidation state of the catalyst. The group relates a shift in the IR band of adsorbed CO to different electron densities in the platinum d-shell. Yoon et al.\cite{78} explain different catalytic activity of Au$_n$ clusters at different sites on magnesia by partial charging of the clusters. Their IR measurement results show a red shift of the CO stretching vibration, which is already predicted by quantum ab initio calculations to originate from increased electron back donation into the $2\pi^*$ antibinding orbital. Recent measurements on charged and uncharged Co, Rh and Ni clusters
Chapter 3. Catalysis on Nanoparticles

with up to 37 atoms in the gas phase have shown comparable results[101].

In the present study an unsupported nickel aerosol catalyst with different charge states is applied to the methanation reaction of carbon monoxide and determine the activation energy by temperature variation. By applying gas phase methods the influence of support material is omitted, which allows to determine the pure influence of charge on activation energies in chemical reactions. The results from this study are compared with measurements of the CO bond strength determined by IR spectroscopy from carbonyl species and on CO adsorbed on supported catalyst.

3.2.2. Chemistry

The reaction mechanism of methanation on a nickel catalyst has not been investigated conclusively, yet. Experimental results suggest that chemisorbed carbon monoxide dissociates at the catalyst surface and subsequently hydrogen atoms are added to form methane[73, 102–105]. The catalyzed step is commonly agreed on to be the dissociation of CO and a large number of studies investigated the binding energy of CO on nickel and platinum surfaces[71, 99, 106–109]. The rate limiting step of the catalyzed reaction is unclear. Bengaard et al. [108] have calculated activation energies of the steam reforming reaction of methane based on density functional theory. They obtain different activation barrier values for different crystal faces, which yields different rate limiting steps depending on catalyst configuration.

\[
CO + 3H_2 \rightarrow^{Ni} CH_4 + H_2O
\]  

(3.8)

Sehested et al. [102] describe reaction (3.8) in terms of 5 reaction steps on two types of nickel surface sites (†, †), where both hydrogen and carbon monoxide compete for †-sites, while †-sites are selective for CO.
3.2. Unsupported Catalyst

\[ CO + \dagger \rightleftharpoons CO^\dagger \]  
(3.9)

\[ 0.5 \ H_2 + \dagger \rightleftharpoons H^\dagger \]  
(3.10)

\[ CO^\dagger + \dagger \rightarrow O^\dagger + C^\dagger \]  
(3.11)

\[ C^\dagger + 2 \ H_2 \rightarrow CH_4 + \dagger \]  
(3.12)

\[ O^\dagger + H_2 \rightarrow H_2O + \dagger \]  
(3.13)

The equilibrium reactions (3.9) and (3.10) are defined by rate constants \( K_{CO} \) and \( K_{H_2} \) with activation energies of 122kJ/mol and 43kJ/mol respectively. The rate determining step is the dissociation of CO (3.11), while reactions (3.12) and (3.13) are fast.

Polizzotti and Schwarz [104] found that the surface ratio of CO and \( H_2 \) changes with temperature and total pressure of the reactants in favor for hydrogen at high temperatures and high partial pressures, which leads to a change in activation behavior. At low temperatures the activation energy is in the range of 90kJ/mol and changes to values around 60kJ/mol at high temperatures.

Seipenbusch [94] has measured activation energies of 96kJ/mol at low temperatures and 38kJ/mol at higher temperatures on unsupported aerosol catalysts with uncontrolled charge state. The results have been confirmed by Weber et al. [95] for the same reaction conditions.

3.2.3. Catalyst Material

The catalyst material was produced as nanoparticulate aerosol by a spark generator (SG) according to Schwyn et al. [110]. A high voltage between two electrodes of the desired catalyst material triggers a spark, which locally heats the electrode surface to a temperature of several thousand Kelvin, causing the electrode material to evaporate explosively. A constant inert gas stream is passed between the electrodes to rapidly cool the vapor. High supersaturations are achieved and primary nanoparticles are formed, which agglomerate to flaky, high surface area fractal-like structures.

Figure 3.9 shows a typical size distribution as obtained from the spark generator under conditions used in this experiment. The mode represents...
agglomerates of primary particles in the size range between 2nm and 5nm. Figure 3.10 (left) shows an electron micrograph of the particles before entering the reactor.

In the plasma channel of the spark, positive and negative ions are formed of which some escape recombination and attach to particles. The ion concentration is high enough to ensure a Boltzmann charge distribution [40]. In this case this results in a stable ratio of \( \approx 29\% \) neutral particles, 32\% positively charged particles and 39\% negatively charged particles. Multiple charging does occur but can be neglected in this case.

Nitrogen adsorption (BET) analysis yielded a specific surface area of 145 m\(^2\)/g for spark generated nanostructured nickel. Assuming spherical particles with 100\% accessible surface, the specific surface area ranges between 168.5 m\(^2\)/g for 2nm particles and 67.4 m\(^2\)/g for 5nm particles based on bulk density. The surface is thus highly accessible for gas phase reactions.

On the right side of figure 3.10 the catalyst material is shown after passing through the reactor where they are exposed to temperatures up to 728K. The structure of the particles is strongly modified, but no significant
3.2. Unsupported Catalyst

Figure 3.10.: Micrographs showing nickel agglomerates as used in the experiments. Before the reaction (left) and after the reaction (right)

differences between charged and uncharged particles were observed. It is assumed that the structural changes are independent of charge, so that changes in the catalytic activity through surface modifications are also charge-independent.

Magnusson et al. [25] reported charge inversion from the positive to the negative polarity for 15nm gold and tungsten particles at temperatures above 873K. To ensure charge stability the average charge of the aerosol was measured for different particle charge states before and after the reactor. Figure 3.11 shows the ratio of charged particles before and after the reactor. At temperatures between 673K and 728K no changes in charge were observed for positive and neutral particles, while negative particles are partially decharged. At high temperatures up to 20% of the negative particles loose their charge. Measurements of the total aerosol show a small negative net charge and also reflect the trend towards fewer negative charges at higher temperatures.

3.2.4. Setup

The activation energy was determined by measurement of the temperature dependent product concentration for different charge states of the
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Figure 3.11.

Ratio of particle concentrations before and after the reactor for different particle types. Neutral and positive particle concentrations are unaltered, while negative particles decharge. This effect is also reflected in the total aerosol measurement.

A mass flow controller fed nitrogen (99.99% purity) at a flow rate of 1slpm into the spark generator to produce the catalyst aerosol. In a first experiment the setup shown in the top part of figure 3.12 was used to measure the activation energy of neutral particles as compared to all particles. The charged particles were removed in a parallel plate electrostatic precipitator (ESP) with a plate distance of \( \frac{1}{4} \) mm. Charge measurements on the aerosol after passing the ESP with an aerosol electrometer (AEM) show significant residual net charge at a precipitation voltage of 6.7kV. The particle concentration was \( 4.4 \times 10^{13} \text{m}^{-3} \) before and \( 1.2 \times 10^{13} \text{m}^{-3} \) after removing the charged fraction.

In a second experiment the influence of particle polarity was determined (figure 3.12, bottom). The aerosol passed through a differential mobility analyzer (DMA, see appendix A), which extracts particles of a given electrical mobility. It was operated with a large ratio of aerosol to sheath air flow (\( Q_a/Q_s = 0.5 \)). This led to a very poor size distribution, but the goal here was to extract a high concentration of charged particles from the aerosol. The polarity of the electric field applied to the classification region determines the polarity of the aerosol selected. The particle concentration was \( 5.59 \times 10^{12} \text{m}^{-3} \) for negatively charged particles and \( 5.27 \times 10^{12} \text{m}^{-3} \) for
3.2. Unsupported Catalyst

Figure 3.12:
Setup for measuring the activation energy of neutral particles (top) and charged particles (bottom) as compared to the total aerosol

positively charged particles. By passing the processed aerosol through an ESP and measuring the remaining particle concentration with a condensation particle counter (CPC), the amount of residual neutral particles was determined to be less than 0.1%. Due to losses in the DMA particle concentrations from the second set of experiments do not coincide with the values obtained from the first. To compare the results, the product concentration was devided by the particle surface area per unit volume.

The preconditioned aerosol catalyst was mixed with the exact gases by mass flow controllers (0.05slpm CO\textsubscript{2} and 0.25slpm H\textsubscript{2}) and fed into a heated wall reactor. The reactor wall is a quartz glass tube of 1 m length and 0.04 m diameter. It was electrically heated and temperature controlled. Figure 3.13 shows the temperature profile of the reactor for the temperatures used in these experiments. The residence time in the heated zone was between 9s and 10s, depending on the reactor temperature. The sharp drop of temperature strongly inhibits the reaction outside the heated zone.

After passing through the reactor the particles were removed from the gas stream by a filter and the processed gas mixture was led into a FTIR-spectrometer (Bruker Vector 22) equipped with a long path gas cell (8m path) allowing to measure methane concentrations down to ppm levels.
3.2.5. Measurement Procedure

Catalytic background activity due to deposited catalyst particles on the walls of the reactor was measured at elevated temperatures. It varied in time due to catalyst poisoning and time dependent measurements were taken to correct for this effect. The gasborne catalyst was periodically removed by switching the spark generator off and on again. An example of the product concentration vs. time is shown in figure 3.14, left. The baseline was fitted by an exponential function with three variables. To obtain the conversion due to the gasborne catalyst, the baseline in figure 3.14 (left) is subtracted from the curves representing the data with the ESP off (all particles) and ESP on (neutral particles). The result is shown in figure 3.14 (right). This method allows to predict the measurement values over several hours of experiment time with an accuracy down to a few parts per million. The same experiment was then performed for different temperatures and the activation energy determined from an Arrhenius-plot.

3.2.6. Results and Discussion

The activation energy of the methanation reaction was determined by varying the reaction temperature between 673K and 723K. The logarithm of the product concentration was plotted against the inverse temperature in an Arrhenius plot (figure 3.15). Table 3.1 shows the respective acti-
3.2. Unsupported Catalyst

Figure 3.14.: Data before (left) and after (right) removing the background. (T=723K)

vation energies. Values for negative particles are not corrected for the change in charge they undergo in the reactor, because the characteristic timescale of decharging is unknown at this point. Based on linear decharging in time, the average charge loss is about 10%, a variation tolerated in these measurements. The striking result is that neutral particles exhibit a much higher activation energy than the charged catalyst particles. Thus charging with both polarities evidently lowers the activation energy significantly.

The activity of the total aerosol catalyst, containing neutral and charged particles roughly according to a Boltzmann distribution, is also compared to the activity of the sum of the independently measured neutral and charged species. For direct comparison it is necessary to correct for the different amounts of catalyst present by normalizing the product concentrations with the surface of the initial material. Within the experimental error good agreement between the measurements is obtained, both with respect to activation energy and total conversion as can be seen from figure 3.16.

For supported catalysts the connection between catalyst charge and activity is largely uninvestigated. However, detailed empirical studies on SMSI for a variety of materials and supports are available. Kester and Falconer [111] have reported that nickel on Al₂O₃ substrates shows two
Chapter 3. Catalysis on Nanoparticles

Figure 3.15.: Arrhenius plot for the methanation on Ni catalyst. Comparison of all particles with respect to the neutral particles (left) and positive and negative particles (right), respectively.

Figure 3.16.: Arrhenius plot for the methanation on Ni catalyst. Surface area normalized rate of reaction compared to the weighed sum of normalized single measurements. Weighing factors according to aerosol composition (32% pos., 39% neg., 29% neut.)
3.2. Unsupported Catalyst

Table 3.1:

<table>
<thead>
<tr>
<th></th>
<th>neutral</th>
<th>negative</th>
<th>positive</th>
<th>all</th>
<th>sum</th>
<th>all</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>148.2±28.7</td>
<td>42.6±35.3</td>
<td>59.7±22.6</td>
<td>50.4±26.5</td>
<td>65.8±19.6</td>
<td>38.1±3.5</td>
</tr>
</tbody>
</table>

Charge dependent activation energy for the methanation reaction of CO on gasborne Ni-catalyst [kJ/mol]. Values for the total aerosol (all) and the sum of components (sum) are given together with values obtained for the total aerosol by Weber et al. [95].

different types of active sites for methanation. Sites of nickel close to the substrate have SMSI and show an activation energy of 145kJ/mol, while nickel sites surrounded by nickel atoms activate CO at 51kJ/mol. Hu et al. [97] report 3 different sites with activation energies of 101kJ/mol, 56.5kJ/mol and 83.1kJ/mol which are obtained from different reduction mechanisms of the catalyst material. Yoon et al. [78] have shown recently that charging of gold clusters by contact potential on magnesium oxide reduces the bond strength of adsorbed CO and influences catalytic activity.

According to Blyholder [107] and Zhou et al. [100] the binding between nickel and carbon monoxide is based on electron donation from nickel into the CO $2\pi^*$ orbital and electron back-donation from the CO $5\sigma$ orbital into the metal. It is quite clear that electron donation into the antibinding $2\pi^*$ orbital weakens the bond to an extent determined by ionization potential and population of the donating metal d-shell. It is assumed that atoms/surfaces with a lower ionization potential donate electrons more readily than materials with higher ionization potential. High electron densities in the d-shell further support electron donation and thus anions are expected to have the lowest CO bond strength. The role of back-donation is much more complicated and up to now it is not completely clear whether a complete electron exchange with the metal or polarization of the CO bond takes place but in most cases polarization can be assumed. The CO $5\sigma$ orbital becomes polarized towards the metal and stabilized with increasing positive charge on the metal, suggesting that cations have the highest CO bond strength. On the other hand, increasing population of the valence s-orbitals in the metal reduces this effect by electrostatic repulsion.
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Extensive infrared spectroscopy studies and density functional theory (DFT) calculations on metal carbonyl molecules have shown that CO bond strength varies strongly between neutral and ionic species[100]. In agreement with this theory an increased activity of the negatively charged catalyst as compared to the neutral material is observed. On the other hand, positively charged catalyst particles show a comparable activity, although measurements on nickel carbonyl have shown increased CO bond strength. The results of single metal atoms are only partly transferable to gasborne particles, since nanoscale materials show significantly different properties with respect to surface morphology and electronic band structure as compared to both atoms and bulk materials.

3.2.7. Conclusions

Different activation energies of 148.2 kJ/mol, 42.6 kJ/mol and 59.7 kJ/mol were measured for particles with neutral, negative and positive charge, respectively. The least active species has only little influence on the total apparent activation energy, which is determined by the active components. This was proven by adding the contributions of the single components according to their respective fraction in the original aerosol with a Boltzmann charge distribution. The result of $65.8 \pm 19.6\, \text{kJ/mol}$ agrees well with the measured activation energy of the original aerosol of $50.4 \pm 22.6\, \text{kJ/mol}$.

It is concluded, that the charged aerosol catalyst has a modified electronic structure which changes the bond strength of chemisorbed CO. Since dissociation of CO is believed to be the rate limiting step in methanation, the apparent activation energy of the reaction is expected to change accordingly. The results are qualitatively understandable by electron donation/back-donation[107].

The activation energies of the charged aerosol catalyst are comparable to values measured on isolated active sites with strong and weak metal surface interaction, respectively. It is suggested that the charge transfer between substrate and catalyst due to the contact potential plays an important role in the phenomenon of strong metal support interaction.
Chapter 4.

Deposition by Focussed Impaction

4.1. Introduction

Bulk nano-materials are often produced by liquid or sol-gel routes because high quantities are achieved. However, the use of solvents requires additional product refining to maintain purity. The final product is typically available in form of suspension or powder and is further handled in standard processes. Through the absence of solvents, aerosol routes are already

Demut
Seh’ ich die Werke der Meister an,
So seh’ ich das, was sie getan;
Betracht’ ich meine Siebensachen,
Seh’ ich was ich hätt sollen machen¹.

(von Goethe [3])

¹Humbleness - As I look at the creations of masters, I see what they have done; As I look at my bits and pieces, I see what I should have done.
Chapter 4. Deposition by Focussed Impaction

much cleaner and additional refining is not required. Process conditions are used to finely tune the product properties and feedback is possible, because continuous production processes are applied. However, often only small quantities as compared to liquid phase routes are obtained at high quality. For equally sized particles, no large scale standard processes exist for aerosols. Aerosol materials and processes thus must be developed in parallel for successful implementation in new products.

Aerosol deposition by patterned impaction from micronozzles was first applied by Kashu et al. [112] for particles with diameters less than 100nm. The system was applied and improved for the production of piezo-ceramics for free forming, insert molding and mask deposition by Akedo et al. [113]. Because of the small nozzle dimensions the nozzle walls must be heated to avoid clogging. To grow structures with a large aspect ratio they move the nozzle up along with the structure.

The use of a focusing impactor allows to concentrate the aerosol into a thin beam far away from the nozzle walls, thus clogging poses no problem. Coupled with a manipulator stage to move the impaction plate micrometer sized functional structures can be produced directly from aerosols [114, 115]. With the present system it is possible to deposit useful quantities within minutes, which showed distinct nanoparticle properties acting as gas sensing material. The structure of the material is comparable to results obtained by Akedo [116]. The deposition method is thus not completely new.

The present study was carried out because it was realized that the combination of this method with a flexible way of producing nanoparticles has great potential in view of of various applications including chemical sensors, catalysis, lithium ion batteries and solar cells. As examples towards the specific application of chemical sensors, the materials were tested with respect to gas adsorption and electrical conductivity. It was possible to show the transition from distinct nanoparticle behavior to bulk response with increased sintering between the particles.

4.2. Aerodynamic Focusing and Impaction

Both aerodynamic focusing and impaction are processes using the inertia of the particles. The particles are focused by contracting and subsequently
4.2. Aerodynamic Focusing and Impaction

expanding the aerosol stream in an orifice while maintaining laminar flow. While the gas quickly relaxes to the tube walls behind the orifice, the particles remain in the center of the flow due to their inertia (figure 4.1). For impaction the aerosol stream exits a nozzle at high velocities and is bent sharply over a flat plate. The particles do not follow the gas streamlines and impact onto the surface.

Since both aerodynamic focusing and impaction are inertial processes the obtained diameters are either the Stokes diameter $d_s$ or the mass equivalent diameter $d_m$. A more detailed explanation on measurements and diameters can be found in appendix C. For particles and carrier gas dimensionless numbers are introduced to describe the dynamic properties with respect to bends or obstructions on different scales.

The Reynolds number is the ratio between inertial forces and friction forces and defines if the flow regime is laminar or turbulent. It is defined for gas streams ($Re_g$) and particles ($Re_p$) by
Chapter 4. Deposition by Focussed Impaction

\[ Re = \frac{F_{\text{inertial}}}{F_{\text{friction}}} \]
\[ Re_g = \frac{\rho_g v_{rel} d_c}{\eta_g} \]  \( (4.1) \)
\[ Re_p = \frac{\rho_g v_{rel} d_V}{\eta_g} \]  \( (4.2) \)

where \( F_{\text{inertial}} \) and \( F_{\text{friction}} \) are inertial and frictional forces and \( \rho_g \) and \( \eta_g \) are the density and viscosity of the gas, respectively. \( v_{rel} \) is, in case of the gas stream Reynolds number, the relative velocity of gas with the structure of characteristic diameter, \( d_c \), through or around which the gas flows. In case of the particle Reynolds number it is the relative velocity between the gas stream and a particle diameter \( d_v \).

For spherical particles the particle Reynolds number is related to the volume equivalent diameter, which corresponds to the physical diameter of the particle. Non-spherical particles are much more difficult to treat in a model with respect to flow properties, because they show different characteristic dimensions depending on the scale on which the particle is looked at. A porous particle for example is smooth on large scale while it is rough on small scale. Depending on the point of view the flow regime thus largely differs as well. A flow is considered laminar if the gas Reynolds number is lower than 2000 and considered turbulent if it is larger than 4000. For particles the regime is laminar for particle Reynolds numbers smaller than 1 and increasingly turbulent if larger.

Besides the flow properties the inertial properties of particles in a fluid are of great interest, mainly to determine whether a particle follows the fluid streamlines or not. The distance for a particle to stop due to frictional forces is called stopping distance and is in the laminar flow regime \( (Re_p < 1) \) related to the momentum of the particle via:

\[ S_p = B m_p v_{rel} \]  \( (4.3) \)

with \( S_p \) being the particle stopping distance, \( B \) and \( m_p \) the mechanical mobility and mass of the particle and \( v_{rel} \) the relative velocity between particle and gas stream, respectively.
### 4.2. Aerodynamic Focusing and Impaction

The term stopping distance can be misleading although straightforward from definition, because the particle does not necessarily stop. Just the relative velocity between gas and particle becomes zero. A better term would be relaxation distance, thus the distance a particle needs to "relax" to the fluid streamlines. It then is defined as the distance a particle travels before following an (uncurved) streamline. The time for a particle to travel the stopping distance is called stopping time or relaxation time, respectively.

The Stokes number

\[
Stk = \frac{S_p}{d_c} = \frac{Bm_p v_{rel} d_c}{d_e}
\]  \hspace{1cm} (4.4)

is defined as the ratio between the relaxation distance and the characteristic diameter\(^2\) of an obstacle as shown in equation (4.4). It indicates if a particle can follow the gas streamlines around the obstacle \((S_p \ll d_c \Rightarrow Stk \ll 1)\) or if it will change streamline or impact on the obstacle due to its inertia \((d_c \ll S_p \Rightarrow Stk \gg 1)\). The Stokes number is thus critical for aerodynamic focusing and impaction alike.

To calculate the focusing performance of the focusing system with respect to different flow rates and particle sizes the model of Wang et al. \[117\] is followed. The following equation derived from Epsteins mobility model for the Stokes number of a particle passing through an aerodynamic lens is used:

\[
Stk = \frac{1}{\left(1 + \frac{\pi a}{2} \sqrt{2 \pi \gamma^3}\right)^{8/3} m_g \rho_d d_m c^2} 8 \rho_{\text{g}} r_{\text{n}}^2
\]  \hspace{1cm} (4.5)

Based on the particle Stokes number the performance of an aerodynamic lens system can be calculated, if pressure drop and dimensions are known. According to Liu et al. \[118\] the optimum Stokes number for focusing is in the range of 1 for a thin plate lens.

After exiting the focusing system, the gas flow is deflected 90° by a flat substrate. Depending on the Stokes number with respect to nozzle radius and exit velocity, the particles are either carried away with the gas

\(^2\)Instead of defining Stokes’ number on a length scale it sometimes is defined on a time scale. It then is the ratio of stopping/relaxation time to the characteristic time, e.g. the time a particle needs to pass an obstacle.
Chapter 4. Deposition by Focussed Impaction

stream or impact on the substrate. 50% impaction probability is obtained at \( Stk_{50} = 0.24 \) [119]. If exit velocity, particle mass and nozzle diameter are known, the cutoff diameter is calculated via

\[
d_{cut} = \sqrt{C_v} = \left( \frac{18\eta \eta_n Stk_{50}}{\rho_p \nu_e} \right)^{\frac{1}{2}} = \left( \frac{18\pi \eta \eta_n^2 Stk_{50}}{\rho_p Q_i} \right)^{\frac{1}{2}},
\]

(4.6)

where the slip correction is calculated downstream.

4.3. Experimental Setup

The setup consists of three major parts: Firstly the particle production, measurement and conditioning system, secondly the impaction system and thirdly the gas inlet and electrical measurement system. Figure 4.2 shows the flow scheme of the setup.

For the present experiments the particles were produced by spark generation, as already described in chapter 3.2.3. The instrument used in this setup is an adapted commercial soot generator\(^3\) (SG), operated with metallic electrodes in a nitrogen atmosphere. The major part of the aerosol is released through a filter in the fumehood and only a small quantity is used for further classification and impaction.

The following components, a differential mobiliy analyzer (DMA)\(^4\), an aerosol electrometer (AEM) and impactor can be combined to achieve different goals. By directly feeding the spark generator output into the AEM, the total aerosol concentration can be estimated from the charging dynamics of the production process. As described in chapter 3.2.3 the charge on the aerosol is close to a Boltzmann distribution but slightly asymmetric with respect to polarity, and the AEM measures the net charge, the difference between positive and negative charge (see chapter 1). The measured current accounts for approximately 7% of all particles. The DMA can be used for mobility distribution measurements and size selection, depending on which instrument follows. Additional conditioning steps (e.g. sintering) can be implemented between spark generator and DMA or DMA and impactor if necessary.

\(^3\)Palas, Aerosol Generator GFG-1000
\(^4\)TSI short, see table A.1

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4.3. Experimental Setup

Figure 4.2: Flow scheme of the impactor setup for deposition and in-situ measurement of conductive properties of nanoparticle lines (left). Drawing of the impactor vessel with movable substrate (right).
Chapter 4. Deposition by Focussed Impaction

The aerosol is admitted into the focusing impactor through a critical orifice to limit the mass flow. The impactor itself is made of a stainless steel tube that contains an aerodynamic focusing system. The best performance for the palladium aerosol was found with 5 thin plate orifice lenses with 3.8 mm diameter spaced 45 mm apart. The inner width of the impactor is 19 mm and the total length is 225 mm. The ratio between nozzle diameter and distance to the impaction plate was 1 in all cases.

Following the paper of Wang et al. [117] the pressure drop across the aerodynamic lenses was calculated at different mass flow rates based on the experimentally obtained flow rates and base pressures. From there the contraction factor was estimated based on their fitted relationship between particle Stokes number (equation (4.5)) and the near axis contraction factor (figure 4.3).

It can be seen that contraction of the beam is increased with increasing mass flow rate. Opposed to this numerical prediction in these experiments it was found that the focusing increased with decreasing flow rate. This is due to the dependence of the contraction factor on the Reynolds number which is neglected in this calculation and a base pressure in the range of the minimum required pressure. This also explains why the best performance of the impactor was measured after increasing the base pressure to 250 Pa at an aerosol flow rate of 0.107 slpm. The lens Reynolds number in this case is 42, close to the optimum of 70 determined experimentally by van Laarhoven [120].

The impactor reaches into the impactor vessel shown in figure 4.2 (right). It is evacuated by a rotary vane pump to a few millibars, depending on the aerosol flow rate. The particles impinge on a substrate supported by a movable substrate holder, which is moved by a stepper motor in x-direction. Y- and z-position are controlled manually. For conductivity measurements aluminium electrodes of several 100nm thickness were deposited by thermal evaporation on standard microscopy cover glasses (see figure 4.4). The two inner electrodes are connected via BNC-connections to the outside of the impactor vessel. One is connected to a constant voltage supply, the other to a sensitive electrometer. This allows to measure the in-situ resistance and current/voltage characteristics of the deposited material with set voltage and measured current. In combination with the gas mixing system consisting of two massflow controllers, the electric response of the deposited particle bridge with respect to different gas
4.3. Experimental Setup

Figure 4.3.: Contraction factors of an aerodynamic focusing system dependent on the number of lenses and at different flow rates, based on the explanations of Wang et al. [117]. Parameters: (aerosol flow [slpm]/base pressure [Pa]) (0.374/40), (0.289/20), (0.226/1), (0.107/250).
4.4. Results

4.4.1. Material Structure

Polydisperse palladium nanoparticles were impacted on metallic and ceramic substrates. In both cases structures similar to those of Akedo et al. [113] and Di Fonzo et al. [114] were obtained. With the present setup it was possible to form towers when depositing on the same spot for a long time and lines of different height, when scanning the substrate at different speeds.

When depositing towers their outside shows a pinecone like structure as shown in figure 4.5 (top and middle right). Less cohesion in radial than in axial direction leads to fiber formation along the axis of impaction. Figure 4.5 (bottom right) shows a broken tower after sputtering gold to increase conductivity. The fibers or flakes are bent outward by electric forces in a flower like pattern, an effect often observed on this material.

The formation of fibers is also reported by Akedo [116] on deposition from micronozzles. Their explanation is based on the shadowing effect [121], which means that parts of the substrate are shadowed by already deposited particles if the angle of incidence is not perfectly perpendicular to the deposition surface. This leads to the formation of voids and chan-
Figure 4.5:
Micrographs of palladium agglomerates deposited in lines (left) and towers (right). The fibrous structure of the deposited material is clearly visible.
nels, which ultimately results in fibrous structures. However, if this model describes the processes in particle impaction, columns along the direction of incidence are expected, leading to a preferred orientation depending on the angle of incidence. The rotational symmetry found in the towers can thus not be explained by this effect, since the substrate had a fixed position.

The fibrous structure is supposedly due to partial sintering of the particles along the axis of impaction. The kinetic energy is partly dissipated as heat on impact, cleaning the surface from adsorbates and locally melting the particles. The contact of pure metal surfaces leads to atomic contact and cold welding of the materials. Figure 4.6 shows agglomerates before impaction (left) and after impaction (right). Increased neck formation is observed after impaction. The outer shape of the towers is presumed to be defined by abrasion in the particle beam. This is supported by large pieces of debris in the vicinity of the impaction site.

The left column of figure 4.5 shows a line of towers deposited closely to each other by moving the substrate. A regular pattern of cracks is observed. The inside of the material already has the same fibrous structure as observed on larger towers, although the outside still seems smooth. The structure most likely reconfigures after impaction and shrinks. This leads to cracking if the adhesive forces to the substrate are larger than the cohesive forces in the material. In some cases, when large towers were grown in a line, the impactor material peeled off the substrate and curled up. In these cases the cohesive forces of the material were stronger than the adhesive forces to the substrate.

The specific surface area was measured according to Brunauer-Emmett-Teller (BET) from krypton adsorption and obtained a value larger than 100 m$^2$/g. This is close to the maximum value obtained from monodisperse, unsintered particles 5 nm in diameter. It is concluded, that large areas of the surface are accessible to gases in the impacted material, making it particularly suitable for applications requiring gas adsorption as e.g. catalysis or gas sensing.

4.4.2. Conductive Properties

As described above aluminium electrodes were connected to palladium nanoparticle lines to measure their conductivity. Figure 4.7 (left) shows
Figure 4.6: TEM micrographs of palladium agglomerates produced by spark generation before (left) and after (right) impaction. Besides a porous structure neck formation is observed.
the time evolution of the conductivity over several minutes after deposition. A steady increase indicates the formation of new particle-particle connections along the line. This can be explained by the measurement current, through which interparticle contacts with high resistivity are heated, which leads to sintering. This improves the electrical connection and interparticle resistance decreases. Assuming the bulk value of $10^{-7}$ $\Omega$m for the specific resistivity of the particles, the resistance measured corresponds to a wire with a cross section of approximately $1.5 \cdot 10^{-17}$ m$^2$ corresponding to 4x4 nm and increased to 6x6 nm after approximately 500 s. By passing a controlled current for a given amount of time the resistivity of the bridge can be controlled and the conductive properties can be tailored.

A palladium nanoparticle bridge was exposed to 5 Vol% hydrogen gas and measured the conductivity in-situ. The response is shown in figure 4.7 (right). When exposed to the gas for the first time the conductivity increases by a factor of 30. As the gas is removed by evacuating the impactor vessel the conductivity steeply increases by almost four orders of magnitude. In the following exposure/evacuation cycles the conductivity
4.5. Conclusions

drops by more than three decades on exposure to hydrogen and returns
to the original value in a reproducible manner.

As already mentioned above the deposited material is strongly bound
in the direction of impact and much looser in radial direction. The latter
determines the conductive properties of the line. On exposure to hydrogen
the palladium particles swell in forming the hydride and more interpar-
ticle connections are formed. The total contact area along the line is
increased explaining the initial rise in conductivity. This agrees well with
results obtained by Favier et al. [7] on mesowire arrays produced by elec-
trodeposition. It is expected that the measurement current then leads to
formation of permanent bonds between the particles by local heating and
sintering. On evacuation, the conductivity of palladium metal is restored,
which is higher than of palladium hydride. When exposed to hydrogen
again the conductivity drops and the properties of bulk palladium hy-
dride are observed, a behavior already reported by Volkening et al. [122]
on pellets of compacted nanoparticle powder.

It is remarkable that the conductivity changes by four orders of magni-
tude within seconds. This rapid change is attributed to the good acces-
sibility of the surface through the porous structure and the small size of
the particles, which leads to short diffusion paths to and inside the parti-
cles. The material is thereby capable of changing quickly to a large extent
throughout the entire deposit, which results in the observed, extreme rates
of change.

4.5. Conclusions

With the impactor setup at the present stage it was possible to concentrate
a polydisperse aerosol into a beam of several tens of micrometers. By
depositing in one spot, "towers" with an aspect ratio of 10 were produced
at base diameters of about 100 μm. By scanning the substrate with a
stepper motor at different speeds "lines" of ≈100 μm width and variable
height were deposited. The material shows fibrous structure along the
axis of impact due to sintering and much less cohesion in lateral direction.
This leads to a characteristic pinecone-like appearance. The material is
porous with a surface area (BET) of 100 m²/g for palladium. This value
is comparable to the total surface area of monodisperse particles with a
volume equivalent diameter of 5nm.

The impacted material restructures after impaction and shrinks. In particle lines this leads either to cracks in the surface of the material or to detachment from the substrate, depending on the ratio between adhesive and cohesive forces. When passing current through a line of particles, sintering along the line (radial) occurs depending on current and exposure time. When exposed to hydrogen palladium nanoparticles initially show an increasing lateral conductivity explainable by an increase of particle-particle contact induced by hydride formation. Afterwards the material behaves like palladium nanowires, which decrease their resistivity when forming the hydride. The results of the conductivity measurements and the structural analysis support each other with respect to material behavior.

The use of a four-probe measurement system supplying a constant current would allow higher accuracy of the measurement. Two contacts are used to supply the current and two probes are used to measure the voltage drop over a defined length of nanoparticle line. The measurement method allows fine control of the measurement current, which enables to study the sintering behavior in lateral direction in more detail.

It is remarkable that the drastic reproducible change in conductivity induced by hydrogen takes place at room temperature and that a very small quantity of palladium (1ng or smaller) is, in principle, sufficient to make a chemical sensor for hydrogen that can be operated at room temperature.
Summary

of the Thesis
Production and Deposition of Well Defined Aerosol Nanoparticles
for Studies on Basic Properties

by Christian Peineke

... and all that fuss for two pounds of human brain ...

(Adams [123])

The introduction of aerosol technology into industrial application is strongly dependent on the availability of process tools to build production lines. To fully exploit the advantages of aerosol processes with respect to purity, process and product control the different process steps must be thoroughly understood. Although the amounts of produced material are still low as compared to bulk chemical methods, current technology is suitable for many tasks in research and (product-)development. A combination of existing process steps is suitable for the production of complete, aerosol-nanoparticle based devices such as gas sensors.

This thesis investigates the glowing wire method for particle production, which forms the initial step of an aerosol process. The method was introduced by Schmidt-Ott et al. [8] and widely applied for research purposes [6, 9–12], but up to today no detailed information was available with
Summary

respect to particle formation, process conditions and suitable materials.

It is shown that nanoparticle formation occurs mostly due to coagulation from the atomic scale and that the mobility distribution can be controlled by changing temperature and inert gas flow rate. A minimum vapor pressure of $P_s(T_m) > 5 \cdot 10^{-3}$ Pa at the melting point of the wire material was found as criterion to form particles measurable with standard aerosol equipment.

A previous study [11] uses the fact that a fraction of the particles is charged, but gives no explanation. In this thesis, the net charge emission from glowing palladium and silver wires was measured and the results modeled based on Hertz-Knudsen, Richardson, Saha-Langmuir and Clausius-Clapeyron equations. Charged impurities, predominantly alkali and earth-alkali metals, are evaporated in the form of positive ions due to surface ionization. At high temperatures, electrons are co-emitted and contribute to the net current. The model agrees well with the experimental data from the current study and re-interpreted data measured by Jeon et al. [29] in vacuum experiments. The aerosol coagulates including charged species and as a result the self-charging efficiency scales with the number of atoms.

At very low vapor densities particles down to atomic size were observed with high-end nano-DMA technology. Especially stable species occur at mobilities related to "magic number clusters", also found in vacuum mass spectroscopic experiments [46, 47, 51]. The combination of GWG and nano-DMA allows to produce and measure these atomic clusters in the gas phase, enabling further use for chemical reactions and deposition. This instrumentation thus allows to link cluster physics and aerosol science. Combined experiments using mass spectroscopy and mobility analysis simultaneously are necessary to conclusively prove the existence of atomic clusters in the gas phase. However, currently no suitable instrumentation exists to determine the mass of atomic clusters at ambient pressure and transfer systems into vacuum have large losses resulting in unrealistic sampling times.

Many applications require clean and well defined particle surfaces. In a previous study Kirsch [4] succeeded in separating nanoparticles according to their shape based on photoemission. Exposure to negative ions and ultraviolet light in an electric field separated the particles according to their mean drift velocity in a gas. This work investigates the limitations
of the technology and aids to the interpretation of the experimental results by analytical and numerical modeling.

It was shown experimentally that gas impurities may avoid separation, but impurity levels do not have to be so low that gas adsorption is suppressed completely. The findings of Kirsch [4], that unaggregated and aggregated particles are separated, are supported and the separation mechanism is shown to be effective also for different operation conditions and somewhat different particle morphologies.

The system is described analytically by transferring the equations used to predict bipolar charging [1412] which is comparable to a path followed by Maisels et al. [61], who describes an aerosol photocharger without an electric field. In the present state the model of the separation stage neglects the feedback between the electric field and the particle charge in calculating the mobility distribution. A Monte-Carlo approach was chosen to include this effect. The models were cross-checked without the feedback effect to yield the same results.

The models were used to study the photoemission behavior of aggregated and unaggregated particles with the same mobility equivalent diameter. The material properties of aggregates were based on basic assumptions. The analytic model yields qualitative results on the charge state but due to the neglected feedback no conclusion with respect to the shape of the mobility distribution could be drawn. The latter was obtained qualitatively from the numerical model. In general, the particles acquired slightly higher charge levels in the simulations than were observed experimentally.

The simulations are based on a variety of parameters, which mutually depend on each other and are not well defined in non-vacuum conditions. It is possible to find a physically reasonable set of parameters which correctly describes the experimental results, but it is unsure if it is the only existing solution. The combination of simulation and experiments, however, enables to qualitatively verify assumptions on particle photoemission properties and can assist in the prediction of particle behavior.

As shown above nanoparticles can be produced and selected easily with specific properties as size, material and surface morphology in the aerosol phase. This production route is specifically suitable for applications where small quantities of high purity are needed. The availability of different materials from the same production process makes aerosol based nanoparticle production especially suitable for material screening e.g. for catalyst re-
Strong size effects, which influence effectivity and selectivity of catalyst materials are already known for a long time. The activation of nanoscale gold for the oxidation reaction of CO \([65]\) or soot oxidation by platinum clusters \([66, 67]\) are just two examples.

In this work gas phase reactions were used to measure the catalytic activity of deposited nanoparticles in microreactors, dependent on an applied electric field, charging the catalyst. Studies on adsorption and bond strength \([68–71]\) and the influence of catalyst support \([72–75]\) are widely available but only few investigations \([76–79]\) relate these effects to electronic structure or charge. Their influence on the catalytic reaction is not yet completely understood.

Two catalyst systems and reactions were tested. An alumina supported platinum catalyst \((Pt/Al_2O_3)\) was applied for the oxidation of hydrogen and a silica supported palladium catalyst \((Pd/SiO_2)\) was used for the hydrogenation of ethene.

For the oxidation reaction of hydrogen a weak dependence on particle charge was found, but no conclusive results were obtained due to anodization effects and high background levels, related to ever present water impurities in the measurement system. The hydrogenation of ethene prevented these problems and a changed reactor design allowed to determine the activation energy of the reaction via Arrhenius-plots. In this case no significant dependence was found. However, changes in overall concentration indicated that the reactor channel changed and thus the field. Improved reactor design and more detailed studies are necessary to conclusively observe the influence of electric fields on heterogeneous catalysis in arbitrary reactions.

Capacitance spectroscopy was used on particle loaded microreactors to fingerprint the electronic structure of the catalyst particles. Deterioration of the signal due to catalyst anodization was observed for the \(Pt/Al_2O_3\) system. The \(Pd/SiO_2\) system did not show any deterioration, but capacitance spectra varied slightly over time and strongly after actual use in a reaction. Since the particles are not fixed to the substrate, they rearrange over time or at elevated temperatures to their lowest energy state. This changes particle-support strength and thus capacitance response.

To avoid the interference of substrate-catalyst interaction with the effects of catalyst charge, unsupported catalyst material was used. As a
model reaction the methanation of carbon monoxide on nickel catalyst was used. The activation energy was measured for different charge states of the catalyst.

Charged catalyst particles showed an apparent activation energy approximately 3 times lower than uncharged particles. It is known from adsorption studies [107] that CO chemisorbes on a transition metal surface by electron interchange and that the bond strength of carbonyls varies with charge [100]. The electron transfer to and from the adsorbate is strongly influenced by charge on the catalyst and changes bond strength in CO, which leads to different apparent activation energies.

It was proven that field and charge dependent studies are possible on supported and unsupported catalyst, produced in the aerosol phase. This leads to better understanding of catalytic processes, which allows to improve catalyst design and to enhance effectivity and sustainability of chemical production processes. It was indicated that the use of microreactor technology and electric fields allows to control catalyst behavior, which is a first step towards controlled, tunable catalysis. The versatility of aerosol production contributes added value through simple and quick production.

Besides material screening and research on basic nanomaterial properties in the gas phase, nanoparticles were deposited by focused impaction to form microstructures. This material was suitable for the investigation of basic interparticle effects as e.g. conduction and palladium nanoparticle structures were successfully applied as hydrogen gas sensing material. Their large surface-to-volume ratio increases the contact area between gas and metal and diffusion occurs in parallel from several surface sites. The short distances lead to high concentration gradients and high diffusion rates. The response time of a nanoparticle based sensor is very high as compared to thin film or bulk sensors.

Electron microscopy on the deposits revealed a fibrous structure of the material. Due to conversion of kinetic energy into heat on impact, nanoparticles preferably sinter along the axis of impaction. In lateral direction these forces are much smaller and connections are less strong. The porous material shrinks after impaction and depending on the ratio between adhesive and cohesive forces the material either cracks at the surface or peels off the substrate.

The initial conductivity in the lateral direction is low but increases when an electrical current flows through the material for a period of time.
Summary

The current locally heats interparticle connections and locally sinters the material.

The conductivity of palladium nanoparticles was monitored while introducing hydrogen gas to the atmosphere. On first exposure the conductivity increases, although palladium hydride has a lower conductivity than metallic palladium. This is due to swelling of the particles which causes an increased number of particle-particle contacts \[^7\]. The measurement current then locally heats these connections which leads to sintering. On removal of hydrogen the conductivity further increases due to the formation of metallic palladium. Repetitive exposure/removal cycles then show a reproducible behavior similar to compacted palladium nanopowder pellets \[^{122}\]. This proves the suitability of nanostructured materials deposited by focusing impaction for the production of gas sensor devices and clears the way for aerosol based production lines.
Samenvatting

behorend bij het proefschrift
Production and Deposition of Well Defined Aerosol Nanoparticles for Studies on Basic Properties
door Christian Peineke

Het toepassen van aerosol technologie in de industriële wereld hangt sterk af van de beschikbaarheid van standaard proces eenheden voor het opzetten van productielijnen. Om alle voordelen van aerosol technologie op het gebied van zuiverheid, proces- en productcontrole volledig te benutten, moeten de verschillende processtappen volledig duidelijk zijn. Hoewel de geproduceerde hoeveelheden nog steeds klein zijn vergleken bij de productie vanuit de vloeibare fase is de bestaande technologie geschikt voor gebruik in onderzoek en (product-)ontwikkeling. Met een combinatie van bestaande proces eenheden kunnen al complete op aerosol-nanodeeltjes gebaseerde onderdelen, zoals gassensoren, geproduceerd worden.

Dit proefschrift onderzoekt de gloeidraadmethode voor deeltjesproductie als eerste stap in een aerosol productieproces. De methode is geïntroduceerd door Schmidt-Ott et al. [8] en is sindsdien vaak gebruikt voor onderzoek [6, 9–12], maar tot vandaag was er geen gedetailleerde informatie beschikbaar ten opzichte van deeltjesvorming, procescondities en geschikte materialen.

Er is aangetoond dat nanodeeltjes hoofdzakelijk gevormd worden door coagulatie vanaf atomaire schaal en dat de mobiliteitsverdeling door het veranderen van temperatuur en gas-debiet gecontroleerd kan worden. Een minimale gasspanning van $P_s(T_m) > 5 \cdot 10^{-3}$ Pa bij het smelt punt van het draadmateriaal is vereist om deeltjes te maken die met standaard aerosol technieken meetbaar zijn.

Een voorgaande studie [11] maakt gebruik van het feit dat de deeltjes uit de draadgenerator gedeeltelijk opgeladen zijn, maar geeft daar
Summary in Dutch


Bij zeer lage dichtheden worden met high-end nano-DMA technologie deeltjes tot atomaire grootte gemeten. Bijzonder stabiele soorten treden op bij mobiliteiten die gerelateerd zijn aan "magic number clusters"die ook in massaspectrometrische metingen voorkomen [46, 47, 51]. De combinatie van GWG en nano-DMA maakt het mogelijk deze atomaire clusters in de gasfase te produceren en te meten, waardoor verder gebruik voor bijvoorbeeld chemische reacties mogelijk wordt. Deze instrumenten leggen dus een verband tussen clusterphysica en aerosolwetenschap. Gecombineerde experimenten die gelijktijdig massaspectroscoopie en mobiliteitsanalyse toepassen, zijn nodig om het bestaan van atomaire clusters in de gasfase aan te tonen. Momenteel bestaan er echter geen geschikte instrumenten om de massa van atomaire clusters bij omgevingsdruk te meten en transversystemen in het vacuum hebben zulke grote verliezen dat de nodige meettijden onrealistisch zijn.


Het is experimenteel aangetoond dat gasvormige onzuiverheden scheiding kunnen voorkomen, maar dat het zuiverheidsniveau niet noodzakelijk zo laag hoeft te zijn dat adsorptie compleet voorkomen wordt. De ontdekking van Kirsch [4] dat geaggregeerde en niet geaggregeerde deeltjes
gescheiden worden, wordt door resultaten uit deze studie ondersteund en het wordt aangetoond dat het scheidingsmechanisme ook bij enige verandering in omstandigheden en deeltjesmorphologien effectief is.

Het systeem wordt analytisch beschreven door de vergelijkingen over te nemen die toegepast worden om bipolare oplading te voorspellen [124]. Deze aanpak is vergelijkbaar met de methode die gebruikt wordt door Maisels et al. [61], die een aerosol photocharger zonder elektrisch veld beschrijft. In de huidige staat verwaarloost het model van de scheidingsvoorziening de terugkoppeling van het elektrische veld op de deeltjeslading voor de berekening van de mobiliteitsverdeling. Een Monte-Carlo aanpak was gekozen om ook met dit effect rekening te houden. Beide modellen zijn tegen elkaar getest zonder terugkoppeling en leverden dezelfde resultaten.

De modellen zijn vervolgens gebruikt om de photoemissie-eigenschappen van geaggregeerde en niet geaggregeerde deeltjes met dezelfde mobiliteitsdiameter te bestuderen. De materiaaleigenschappen van aggregaten zijn gebaseerd op fundamentele aannamen. Het analytische model levert kwalitatieve resultaten over de ladingstoestand maar omdat er in dit geval geen rekening is gehouden met de terugkoppeling, kan er geen conclusie getrokken worden ten opzichte van de vorm van de deeltjesverdeling. Deze wordt kwalitatief geleverd door het numerieke model. In het algemeen berijken deeltjes in de simulaties lichtelijk hogere ladingen niveaus dan in de experimenten.

De simulaties zijn gebaseerd op een aantal parameters die allebei van elkaar afhangen en buiten het vacuum niet goed gedefinieerd zijn. Er bestaat een set van fysically zinvolle parameters die de experimentele resultaten correct beschrijven, maar het is onzeker of dat de enige mogelijke oplossing is. De combinatie van simulaties en experimenten maakt het mogelijk de aannames ten opzichte van deeltjesphotoemissie kwalitatief te verifiëren en kan helpen deeltjesgedrag te voorspellen.

Zoals eerder aangetoond, kunnen nanodeeltjes makkelijk met specifieke eigenschappen zoals grootte, materiaal en morphologie van de oppervlakte in de aerosol fase geproduceerd en geselecteerd worden. Deze productiemethode is bijzonder geschikt voor toepassingen die kleine hoeveelheden met hoge zuiverheid vereisen. De beschikbaarheid van verschillende materialen uit hetzelfde productieproces maakt de aerosol gebaseerde productie van nanodeeltjes bijzonder geschikt voor material screening in catalysatoronderzoek.
Grote effecten van de deeltjesgrootte op de effectiviteit en selectiviteit van catalysatormaterialen zijn al lang bekend. De activatie van nanoschalig goud voor de oxidatie van CO \[65\] of de roetoxidatie door platinum clusters \[66, 67\] zijn daar maar twee voorbeelden van.

In dit proefschrift worden reacties in de gasfase gebruikt om de catalytische activiteit van in microreactoren neergeslagen nanodeeltjes ten opzichte van door een extern elektrisch veld geïntroduceerde lading te meten. Onderzoek ten opzichte van bindingssterkte \[68–71\] en de invloed van de catalysatordrager \[72–75\] zijn op grote schaal verkrijgbaar, maar weinige studies relateren deze effecten aan de electronische structuur of lading \[76–79\] en de invloed op de catalytische reactie is nog niet duidelijk.

Twee materiaalssystemen en reacties worden getest. Een alumina gedragen platinum catalysator (\(\text{Pt/Al}_2\text{O}_3\)) was toegepast op de oxidatie van waterstof en een silica gedragen palladium catalysator (\(\text{Pd/SiO}_2\)) was toegepast voor de hydrogenatie van etheen.

In het geval van de oxidatie van waterstof wordt een zwakke afhankelijkheid van de reactierate van de deeltjeslading gevonden, maar de resultaten waren onduidelijk door anodizatieeffecten en een hoge achtergrondruis door altijd voorkomende watervervuiling in het meetsysteem. Het gebruik van de hydrogenatiereactie van etheen vorkomt deze problemen en een veranderd reactordesign maakt het mogelijk de activeringsenergie van de reactie via Arrhenius-grafieken te bepalen. In dit geval wordt er geen significante afhankelijkheid van de reactierate op de deeltjeslading gevonden. Veranderingen in de totale concentratie aan de andere kant laten vermoeden dat het reactorkanaal is veranderd en daardoor ook het elektrische veld. Een verbeterd reactordesign en gedetailleerdere studies zijn nodig om de invloed van het elektrische veld op heterogene catalyse in willekeurige reacties te bestuderen.

Capacitance spectroscopy wordt op microreactoren met gedeondeerde nanodeeltjes toegepast om de electronische structuur van de catalysator-deeltjes te fingerprinten. Verslechtering van het signaal door anodisatie van de catalysator werd geregistreerd bij het \(\text{Pt/Al}_2\text{O}_3\) systeem. Het \(\text{Pd/SiO}_2\) systeem vertoonde deze verslechtering niet, maar de capaciteit-spectra veranderden lichtelijk met de tijd en sterk door daadwerkelijk gebruik in een chemische reactie. Omdat de deeltjes niet aan het substraat vastzitten vindt met de tijd of bij verhoogde temperatuur een herordening plaats tot de deeltjes het minimum van de oppervlakte-energie beriken,
waardoor de deeltjes-substraat wisselwerking en dus de gemeten capaciteit verandert.

Om wisselwerkingen tussen substraat en catalysator van ladingseffecten te scheiden, wordt ongedragen catalysatormateriaal in de aerosolfase toegepast. De methanisatie van koolmonoxide op nickel-catalysator wordt als modelreactie gebruikt en de activeringsenergie voor verschillende ladingstoestanden van de catalysatordeeltjes gemeten.

De geladen catalysatordeeltjes tonen een ca. 3 keer lagere schijnbare activeringsenergie dan ongeladen deeltjes. Adsorptiestudies hebben aangetoond, dat CO door electronenuitwisseling op een overgangsmetaalloppervlak chemisorbeerd en dat de bindingssterkte van carbonylen met de lading verandert [100, 107]. De electronenoverdracht in en uit het adsorbaat is sterk door de lading op de catalysator beïnvloed en verandert de bindingssterkte in de koolmonoxide, wat tot verschillende schijnbare activeringsenergieën leidt.

Het is aangetoond dat veld- en ladingsafhankelijke metingen mogelijk zijn aan gedragen en ongedragen catalysatordeeltjes, die in de aerosolfase geproduceerd zijn. Dit leidt tot beter begrip van catalytische processen en maakt verbeterd catalysatorontwerp voor verbeterde efficiëntie en duurzaamheid van chemische processen mogelijk. Het lijkt er sterk op dat het gebruik van microreactortecnologie en elektrische velden geschikt is om catalysatoreigenschappen te veranderen. Dit is een eerste stap in de richting van gecontroleerde en gecontroleerd veranderbare catalyse. De veelzijdigheid van aerosol-productieprocessen draagt door eenvoudige en snelle productie extra waarde bij.

Onderzoek met electronenmicroscopie liet een fiberachtige structuur van het materiaal zien. Door omzetting van kinetische energie in warmte bij de inslag sinteren nanodeeltjes met voorkeur langs de impactie-as. Deze krachten zijn veel kleiner in laterale richting en de verbindingen worden minder sterk. Het poreuse materiaal krimpt naar impactie en breekt open aan de oppervlakte of laat los van het substraat, afhankelijk van de verhouding tussen adhesive en cohesive krachten.

De initiële geleidbaarheid in laterale richting is laag, maar stijgt als een elektrische stroom voor een bepaalde tijd door het materiaal vloeit. De stroom verwarmt de verbindingen tussen de deeltjes en sintert het materiaal lokaal.

De geleidbaarheid van palladium nanodeeltjes was gemeten tijdens de verhoging van de waterstofconcentratie in de omgevingslucht. Tijdens de eerste blootstelling stijgt de geleidbaarheid, hoewel palladiumhydrid een lagere specifieke geleidbaarheid heeft dan metallic palladium. Door de uitzet van de deeltjes wordt het aantal deeltjescontacten verhoogd [7]. De meetstroom verwarmt vervolgens lokaal de verbindingen wat tot sintering leidt.

Als de waterstof weer uit de omgevingslucht verwijderd wordt, stijgt de geleidbaarheid verder door het ontstaan van metallic palladium. Herhaalde blootstellingscycli tonen dan reproduceerbaar gedrag, vergelijkbaar met geperste palladium-nanopoeder pellets [122], dus verlaging van de geleiding bij blootstelling aan waterstofgas en terugkeer naar de initiële (hogere) waarde bij verwijderen van het gas. Dit bewijst dat in de aerosol-fase geproduceerde nanogestructureerde materialen geschikt zijn voor gebruik als gassensoren en dat bestaande technologie geschikt is om deze te produceren. Daardoor wordt de weg vrijgemaakt voor de inzet van aerosolgebaseerde productielijnen.
Appendix A.

Size Classification

The differential mobility analyzer (DMA) is a standard tool for measuring particle sizes and size distributions of aerosols. It can be used to produce a monodisperse particle stream for further processing. Today several designs are available, featuring aerosol measurement from ions to micrometer sized particles. The drift velocity of a particle or ion in a carrier gas is determined. It is comparable to chromatography, e.g. the electrophoretic separation of DNA fragments. The process is much faster, however, due to the use of a gas as a medium. Most modern instruments are based on the design of Knutson and Whitby, who have published two initial papers [125, 126] on that topic. Good review of electrical aerosol classification have been written by Flagan [127] and Knutson [128].

A.1. The Cylindrical DMA

Following the initial design of Knutson and Whitby [125] a DMA is built in concentric, cylindrical geometry \(^1\) (see Fig. A.1), which allows to maintain a voltage between the outer mantle and the inner rod electrode. Particle free sheath air is introduced through a laminizing grid (flowrate \(Q_{\text{sheath}}\)) into the drift volume. Through a well defined slit a small amount of charged, polydisperse aerosol is introduced (flowrate \(Q_{\text{poly}}\)) into the DMA without disturbing the laminar flow conditions. The particles move with a speed according to their electrical mobility (definition see chapter 2) towards the center electrode. The residence time of a particle is defined

\(^1\) In fact most DMAs used in the DUT-Nanolab are based on this geometry (TSI3070, LDMA and F/SDMA), for dimensions see table A.1
Appendix A. Size Classification

<table>
<thead>
<tr>
<th>DMA</th>
<th>$l_{\text{max}}$</th>
<th>$l_{\text{mean}}$</th>
<th>$l_{\text{min}}$</th>
<th>$r_i$</th>
<th>$r_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDMA/FDMA</td>
<td>116</td>
<td>114</td>
<td>112</td>
<td>9.35</td>
<td>19.6</td>
</tr>
<tr>
<td>Long</td>
<td>366</td>
<td>364</td>
<td>362</td>
<td>9.35</td>
<td>19.6</td>
</tr>
<tr>
<td>TSI long</td>
<td>446.4</td>
<td>444.4</td>
<td>442.4</td>
<td>9.37</td>
<td>19.58</td>
</tr>
<tr>
<td>GDMA</td>
<td>205.3</td>
<td>203.3</td>
<td>201.3</td>
<td>9.35</td>
<td>19.6</td>
</tr>
<tr>
<td>NanoDMA</td>
<td>11.1</td>
<td>10.0</td>
<td>8.9</td>
<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>

Table A.1: Dimensions of the cylindrical DMAs used in the TU-Delft NanoLab

by the length and cross section of the annular flow region in combination with the gas flow by equation (A.2).

\[
\nu_d = \frac{dr}{dt} = B e q \cdot E \\
E_r = \frac{U_{DMA}}{r \ln \left( \frac{r_a}{r_i} \right)} \\
\tau = \int_{r_i}^{r_a} \frac{r \ln \left( \frac{r_a}{r_i} \right)}{Z P U_{DMA}} dr \\
\tau = \int_{0}^{L_{DMA}} \frac{\pi (r_a^2 - r_i^2)}{Q_{\text{sheath}} + Q_{\text{poly}}} dL' \tag{A.1} \\
\tau = \int_{0}^{L_{DMA}} \frac{\pi (r_a^2 - r_i^2)}{Q_{\text{sheath}} + Q_{\text{poly}}} dL' \tag{A.2}
\]

Particles that have the right drift velocity to cross the radial distance between the electrodes in the residence time $\tau$ will be extracted with the monodisperse aerosol stream $Q_{\text{mono}}$ through a thin slit. By plugging (A.1) into (A.2) and solving to $Z P$ yields the mean mobility of the extracted monodisperse aerosol (A.4). All other particles are either removed with the sheath air or deposited on the electrodes. The mean mobility of the extracted aerosol can be changed by setting different values of $U_{DMA}$ while maintaining the other parameters.
A.2. The DMA Transfer Function

To obtain an accurate measurement the influence of the instrument on the measurement has to be considered. For better understanding a measurement with a scanner is used for illustration: If the original picture gets scanned by an ideal scanner the single lines can be reattached and the copy is the same as the original.

In the real case, however, the measurement value contains information from the neighboring regions around the measurement position and the original is not easily recovered (see figure A.1). In other words the resolution of the scanner is limited by the width of the region that influences the measurement value. In case of the scanner the width remains constant independent of the scan position.

Mathematically the information which is included in a measurement (e.g. the width of the scanning range) is expressed in the transfer function $T$ of an instrument, which gives the probability of the original value $O$ to pass through the instrument. It may depend on the measurement position. The measurement value $M$ itself is the convolution of the object with the transfer function of the instrument:
Appendix A. Size Classification

Figure A.2:
Representation of an ideal instrument (top middle) and a real instrument (top right) with the respective measurement results (bottom). On the left the original image is shown.
A.2. The DMA Transfer Function

\[ M(\xi) = \int_{-\infty}^{\infty} O(\bar{x}) T(\bar{x}, \xi) dx, \]  

(A.3)

where \( \xi \) represents a specific measurement position (e.g., a specific line in the example) and \( \bar{x} \) the variable of the object function (e.g., the line number in general). Please note that the functions are written as vectors and thus the original and the measurement can depend on a number of variables. An ideal instrument has the Dirac delta function as transfer function, which obviously yields:

\[ M(\xi) = \int_{-\infty}^{\infty} O(\bar{x}) \delta(\bar{x} - \xi) dx = O(\xi), \]

thus the object value itself. In the non-ideal case it is necessary to deconvolute the measurement values in order to obtain the original object, which is only possible, if the transfer function is known. One way to do this is to use the properties of a transformation, e.g., of the Laplace transformation, under the assumption that all transformed functions exist.

To experimentally obtain the transfer function of a DMA a tandem DMA setup can be used (see Fig. A.3). Two identical DMA’s are used after each other, the first one producing an aerosol of known size distribution \( (O(\bar{x}) = T(\xi)) \) while the other is used to measure it. The measurement value is thus a convolution of the transfer function with itself and can be recovered rather easily.

For a cylindrical DMA the transfer function defined as the probability of a particle with mobility \( Z_p \) entering with the polydisperse flow and exiting with the monodisperse flow can be calculated from its geometry under assumption of axisymmetric, laminar and incompressible flow \([125, 126, 129]\). It is given by:
Appendix A. Size Classification

\[
T_{DMA} = \max \left[ 0, \min \left( 1, \frac{Q_{\text{mono}}}{Q_{\text{Poly}}}, \frac{Q_{\text{sheath}} + Q_{\text{poly}} - 2\pi Z_p \Lambda \cdot U_{DMA}}{Q_{\text{poly}}} \right) \right]
\]

\[
\Lambda = \frac{L_{DMA}}{\ln \left( \frac{Z_p}{Z_{\text{rms}}} \right)}
\]

This yields a trapezoidal transfer function (Fig. A.4) with the mean mobility, half width and relative width given by:

\[
Z_p = \frac{Q_{\text{sheath}} + Q_{\text{mono}}}{2\pi \cdot \Lambda \cdot U_{DMA}} \quad \text{matching flows}
\]

\[
\Delta Z = \frac{Q_{\text{poly}} + Q_{\text{mono}}}{2\pi \cdot U_{DMA} \cdot \Lambda} \quad \text{matching flows}
\]

In the case of matching flows \((Q_{\text{poly}} = Q_{\text{mono}} \ll Q_{\text{sheath}} = Q_{\text{excess}})\) the transfer function becomes triangular:

\[
T_{DMA}(\zeta) = \begin{cases} 
1 + \frac{2Z_p}{\Delta Z} \left( \frac{\zeta}{Z_p} - 1 \right) & \text{if } Z_p - \frac{\Delta Z}{2} \leq \zeta, \\
1 - \frac{2Z_p}{\Delta Z} \left( \frac{\zeta}{Z_p} - 1 \right) & \text{if } \zeta \leq Z_p + \frac{\Delta Z}{2}, \\
0 & \text{elsewhere,}
\end{cases}
\]

where \(Z_p\) has been substituted with \(\zeta\) for readability.

The desired value from a DMA measurement is the particle concentration density function (PCDF)\(^2\). The integral over the PCDF yields the number of particles in the interval of integration, normalized to a given volume, e.g. the number of particles in the mobility interval \([a,b]\) per cubic centimeter. Since the DMA measures the differential mobility distribution, the related PCDF is given by \(\mathcal{O}(\tilde{x}) = \frac{dN}{d\tilde{x}}\) and has the unit \(m^{-1}\).

Plugging in the PCDF and the transfer function (A.7) into the equation

\(^2\)A more detailed discussion of the statistical background is given in appendix C.
for the measurement value (A.3) one obtains:

\[ M(\bar{Z}_p) = \int_{\bar{Z}_p - \Delta Z_p}^{\bar{Z}_p} \left( 1 + \frac{2\bar{Z}_p}{\Delta Z} \left( \frac{\zeta}{\bar{Z}_p} - 1 \right) \right) \frac{dN(\zeta)}{dZ} d\zeta \]

\[ + \int_{\bar{Z}_p + \Delta Z_p}^{\bar{Z}_p + \Delta Z_p} \left[ 1 - \frac{2\bar{Z}_p}{\Delta Z} \left( \frac{\zeta}{\bar{Z}_p} - 1 \right) \right] \frac{dN(\zeta)}{dZ} d\zeta \]

Since the interval of integration is small \((Q_{\text{mono}} \ll Q_{\text{sheath}})\) the mean-value-theorem can be applied and
Appendix A. Size Classification

\[ M(Z_p) = \frac{dN(Z_p)}{dZ} \int_{Z_p - \Delta Z}^{Z_p + \Delta Z} \left[ 1 + \frac{2Z_p}{\Delta Z} \left( \frac{\zeta}{Z_p} - 1 \right) \right] d\zeta \]

\[ + \frac{dN(Z_p)}{dZ} \int_{Z_p}^{Z_p + \Delta Z} \left[ 1 - \frac{2Z_p}{\Delta Z} \left( \frac{\zeta}{Z_p} - 1 \right) \right] d\zeta \]

\[ = \frac{dN(Z_p)}{dZ} \int_{Z_p - \Delta Z}^{Z_p + \Delta Z} T(\zeta) d\zeta \]

\[ = \frac{\Delta Z dN(Z_p)}{2} \]  

The resulting equation

\[ \frac{dN(Z_p)}{dZ} = 2M(Z_p) \frac{\Delta Z}{\Delta Z} = M(Z_p) Q_{\text{sheath}} Q_{\text{mono}} Z_p \]  

(A.8)

yields the desired PCDF in terms of concentration vs. mobility. In order to obtain the same function in terms of e.g. the particle size the variable can be substituted by:

\[ \frac{dN}{dZ_p} = \frac{dN}{dZ} \frac{dz}{dz_p} \quad \text{for infinitesimal intervals} \]

\[ \frac{M(Z_p)}{\Delta d_p} = \frac{\Delta N}{d_p(Z_p) - d_p(Z_p)} \quad \text{for finite intervals, (A.9)} \]

if the relationship between mobility and diameter is known. Especially in case of finite intervals it is helpful to obtain the function \( d_p(Z_p) \). The electric mobility is related to the mechanical properties of a particle by

\[ Z_p = \begin{cases} 0.441 \cdot \frac{q_p \sqrt{k_B T/m_{\text{mon}}}}{\pi d_p^2} & \text{if } d_p \ll \lambda, \\ \frac{q_p}{8 \pi \eta d_p} & \text{if } \lambda \ll d_p. \end{cases} \]  

(A.10)

The "Cunningham slip correction" (A.11) named after E. Cunningham [1, 130] accounts for the slip of the gas molecules on the surface of the particles. It blends the two equations and the result (A.12) is suitable
A.2. The DMA Transfer Function

over a large diameter range from a few nanometers to microns. For small
clusters and ions, however, the mobility has to be corrected additionally
by the collision cross section of the respective carrier gas.

\[ C_c(d_p) = 1 + 2\lambda \frac{d_p}{a_b} \left\{ a + b \exp\left( -\frac{c d_p}{2\lambda} \right) \right\}, \quad (A.11) \]

Although this mobility-diameter relation has an inverse function, it can
not be given in a closed analytical form. Based on the Lagrange-Inversion-
Theorem its series expansion can be calculated. Another way is the ex-
pansion of the exponential function in the mobility equation and inverting
the resulting polynomial. With respect to an application range from 1nm
to 100nm for singly charged particles equation (A.12) has been expanded
to third order and inverted.

\[ Z_p = \frac{q_p C_c(d_p)}{3\pi \eta d_p} \quad (A.12) \]

\[ Z_p = \frac{2a\lambda + 2b\lambda d_p^{-2} + 1 + bc}{\omega d_p - 1} \lambda + 1/4 \frac{bc^2}{\omega \lambda} + \mathcal{O}(d_p) \]

\[ d_p = \frac{-2}{\omega d_p} \sqrt{1 + 2bc - b^2c^2 - 2be^2a + 8Z_p \omega \lambda a + 8Z_P \omega \lambda b}\]

\[ + 2 \frac{\lambda}{-bc^2 + 4Z_P \omega \lambda} + 2 \frac{\lambda bc}{-bc^2 + 4Z_P \omega \lambda} \quad (A.13) \]

\[ \omega = \frac{3\pi \eta}{c} \quad (A.14) \]

The accuracy of the resulting equation (A.13) varies depending on the
parameters \( a, b \) and \( c \). In table A.2 slip correction values are given for dif-
ferent materials and Knudsen number regimes together with the maximum
relative error of equation (A.13) between 1nm and 100nm.

The solution to equation (A.12) can also be found numerically by iter-
ation. In the first step the Cunningham slip correction factor is assumed
to be unity and a first guess diameter is calculated. With this diameter a
new value for the slip correction is obtained, which is used to calculate a
second guess diameter etc. A simple C-routine doing so is shown in figure
A.5.
Appendix A. Size Classification

<table>
<thead>
<tr>
<th>Author and Reference</th>
<th>Material</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>rel.err. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knudsen and Weber</td>
<td>Glass spheres</td>
<td>1.034</td>
<td>0.536</td>
<td>1.219</td>
<td>1.62</td>
</tr>
<tr>
<td>Millikan</td>
<td>Oil drops</td>
<td>1.209</td>
<td>0.406</td>
<td>0.893</td>
<td>0.46</td>
</tr>
<tr>
<td>Allen and Raabe</td>
<td>Oil drops</td>
<td>1.155</td>
<td>0.471</td>
<td>0.596</td>
<td>0.16</td>
</tr>
<tr>
<td>Allen and Raabe</td>
<td>PSL spheres</td>
<td>1.142</td>
<td>0.558</td>
<td>0.999</td>
<td>0.90</td>
</tr>
<tr>
<td>Rader</td>
<td>Oil drops</td>
<td>1.209</td>
<td>0.441</td>
<td>0.779</td>
<td>0.33</td>
</tr>
<tr>
<td>Hutchins et al.</td>
<td>PSL spheres</td>
<td>1.231</td>
<td>0.469</td>
<td>1.178</td>
<td>1.16</td>
</tr>
<tr>
<td>Hinds</td>
<td>Oil and solids</td>
<td>1.17</td>
<td>0.525</td>
<td>0.78</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Table A.2:
Constants used for the Cunningham slip correction factor (A.11) together with the relative error of eqn. (A.13). \( \lambda = 67.3\text{nm} \) and \( \eta = 1.83245 \cdot 10^{-5} \text{Ns/m} \) [1]

double dpfromZ (double mobility, double lambda, double eta)
//calculates diameter from mobility
{
    double accuracy=1e-5; //relative accuracy
    double Cc=1; //slip correction
    double olddp=0; //old diameter
    double newdp=1; //new diameter
    double a=1.142; //Cc constants
    double b=0.558;
    double c=0.999;

    const double charge=1.602e-19;
    const double pi=3.14;

    while(fabs((olddp-newdp)/newdp)>accuracy)
    {
        olddp=newdp;
        newdp=charge*Cc/3/pi/eta/mobility;
        Cc=1+2*lambda/newdp*(a+b*exp(-c*newdp/(2*lambda)));
    }
    return newdp;
}

Figure A.5.: C-Routine calculating particle size from electric mobility
A.3. Multiple Charge Correction

The mobility distribution as obtained from the DMA measurement can be related to the particle size distribution (PSD) only if the relationship \(d_p(Z_p)\) is known. Multiply charged particles occur due to the dependence of the mobility on the particle charge at higher mobilities in the DMA measurement as compared to singly charged particles and have to be corrected for. When the PSD is calculated directly from the mobility distribution the small particle concentration is typically overestimated. Hoppel [129] has published a method to correct for multiple charges iteratively, if the charge distribution on the particles is known.

The particle size spectrum is cut off experimentally by an impactor on the large diameter end (lowest mobility), hence the lowest mobility fraction only contains singly charged particles. In a first estimate it is assumed, that all particles in the measurement are singly charged\(^3\). Based on this first estimate the number of doubly, triply, etc. charged particles is calculated and subtracted from the higher mobilities. Subsequently the new number of singly charged particles is used to calculate a second estimate. Based on the second estimate the number concentration of multiply charged particles is calculated again and so on. Written out he first estimates are\(^4\):

\(^3\)For aerosols of small particles (< 60\,nm) charged by bipolar ion attachment this first estimate already is correct to approximately 1%.
\(^4\)factoring out 1/\(\beta_q(d_p)\) might help for better understanding.
Appendix A. Size Classification

\[ N(d_p(\bar{Z}_p)) \bigg|_{1st} = \frac{2}{\psi_{1a}^1(d_p(\bar{Z}_p))} \cdot \frac{M(d_p(\bar{Z}_p))}{\Delta d_p} \]

\[ N(d_p(\bar{Z}_p)) \bigg|_{2nd} = N(d_p(\bar{Z}_p)) \bigg|_{1st} - \sum_{q=2}^{\infty} \frac{\psi_{1a}^q \left( d_p \left( \frac{\bar{Z}_p}{q} \right) \right)}{\psi_{1a}^1(d_p(\bar{Z}_p))} \cdot N \left( d_p \left( \frac{\bar{Z}_p}{q} \right) \right) \bigg|_{1st} \]

particles with higher charges based on 1st estimate

\[ N(d_p(\bar{Z}_p)) \bigg|_{3rd} = N(d_p(\bar{Z}_p)) \bigg|_{1st} - \sum_{q=2}^{\infty} \frac{\psi_{1a}^q \left( d_p \left( \frac{\bar{Z}_p}{q} \right) \right)}{\psi_{1a}^1(d_p(\bar{Z}_p))} \cdot N \left( d_p \left( \frac{\bar{Z}_p}{q} \right) \right) \bigg|_{2nd} \]

particles with higher charges based on 2nd estimate

It is crucial to choose the measurement points in such way that the mean particle mobility \( \bar{Z}_p \) has corresponding multiples \( (\bar{Z}_p, 2\bar{Z}_p, 3\bar{Z}_p, \ldots) \) at higher mobilities. Only then the necessary values \( N(d_p(\bar{Z}_p/q)) \) are available for correction. Typically the range of measurement is limited by the power supply and the electric strength of the carrier gas, respectively.

A.4. Modes of Operation

Setting a voltage to the center rod of the DMA, waiting for the system to settle and subsequently measuring the particle concentration by hand is a time consuming task. The introduction of computers with AD/DA equipment in the 1980ies shortened the measurement time [see 137, 138] to some minutes per scan. The process is called differential mobility particle sizing (DMPS).

Scanning the voltage continuously through an exponential ramp allows shortening the measurement time to less than one minute, but the data has to be deconvoluted in a different way, because different size ranges overlap and the particle detection typically lags behind the voltage. Many commercial instruments use this scanning particle mobility sizing (SMPS) mode. For further information see Wang and Flagan [139, 140], Endo et al. [141], Collins et al. [142], Talukdar and Swihart [143], Collins et al. [144] and references therein.
Appendix B.

Charging

For many applications it is desired to obtain a charged aerosol with a well defined charge distribution. Depending on the way how the charge is transferred onto the particle, the mechanism and thus the obtained charge distribution differs. The most common way is charging by ion attachment, where the aerosol is exposed to an atmosphere of ions, which attach to the particles by diffusion. The obtained distribution depends on the properties of the ion and the particle, respectively. Photoemission of electrons poses another way of charging: Electromagnetic radiation excites an electron, which escapes from the particle. The charging process is very much dependent on the surface state of the particle in terms of adsorbates, besides the material properties. A third way of obtaining charged particles is by introduction of ions in the production process. This is not charging in the same sense as mentioned before, because it can not be applied to already existing aerosols. Very often the charge distribution is not well defined in these cases because impurities of precursors and carrier gas have strong influences on the generation process.

B.1. Ion Attachment

Aerosol particles can obtain charge from ions present in the gas phase which diffuse to their surface. The charge is transferred to the particle and the neutral gas molecule desorbs again. The ion attachment rate \( \rho_{\text{in}}^{q=\pm 1} \) (equation (B.4)) describes the probability that a particle obtains a charge in unit time at a given ion concentration. It depends on the particle size and charge state as well as the properties of the ions (mobility, mass, speed, etc.). The derivation treats the diffusion regime far away from the
Appendix B. Charging

particle and the free molecular regime close to the particle differently [2]. This accounts for the change of physical laws when the ion passes the last gas molecules in its approach to the particle surface. The distance where the change takes place is called adsorption sphere:

\[ \delta = \frac{r_p}{K_{n_{\text{ion}}}} \left( \frac{(1 + K_{n_{\text{ion}}})^5}{5} + \frac{(1 + K_{n_{\text{ion}}^2})(1 + K_{n_{\text{ion}}})^3}{3} + \frac{(1 + K_{n_{\text{ion}}^2})^{5/2}}{15} \right) \]  

(B.1)

The ion properties enter the ion attachment coefficient through the mean thermal velocity \( \bar{c}_{\text{ion}} \), the diffusion coefficient \( D_{\text{ion}} \) and the ion Knudsen number \( K_{n_{\text{ion}}} \) [145]:

\[ \bar{c}_{\text{ion}} = \sqrt{\frac{8k_B T}{\pi m_{\text{ion}}}} \]  

\[ D_{\text{ion}} = k_B T \frac{Z_{\text{ion}}}{e} \]  

\[ \lambda_{\text{ion}} = \begin{cases} \frac{3 D_{\text{ion}}}{\bar{c}_{\text{ion}}} & \text{for } m_{\text{ion}} \ll m_{\text{gas}} \\ 1.67 \frac{D_{\text{ion}}}{\bar{c}_{\text{ion}}} & \text{for } m_{\text{ion}} \approx m_{\text{gas}} \\ \frac{32 m_{\text{gas}} D_{\text{ion}}}{3 \pi m_{\text{ion}} \bar{c}_{\text{ion}}} & \text{for } m_{\text{ion}} \gg m_{\text{gas}} \end{cases} \]  

\[ K_{n_{\text{ion}}} = \frac{\lambda_{\text{ion}}}{r_p} \]

\( \lambda_{\text{ion}} \) as given above is derived by Huang and Seinfeld [146] and an approximated solution for binary diffusivity. However, up to today many different formulas are in use. The solution given by Fuchs and Sutugin [147] (equation B.2) is often used e.g. by Reischl et al. [148] and will be applied throughout this work to be consistent. A slightly modified version is used e.g. by Adachi et al. [40] and by Biskos et al. [145].

\[ \lambda_{\text{ion}} = \frac{16 \sqrt{2} D_{\text{ion}}}{3 \pi \bar{c}_{\text{ion}}} \left( \frac{m_{\text{gas}}}{m_{\text{gas}} + m_{\text{ion}}} \right) \frac{1}{2} \]  

(B.2)

In order to describe the path of the ion inside the diffusion sphere some geometrical parameters are needed:
B.1. Ion Attachment

Table B.1:
Attachment coefficients for the attachment of negative ions as function of particle charge and size. \( m_{\text{ion}} = 60 \text{ amu}, Z_{\text{ion}} = 2.15 \times 10^{-4} \text{m}^2 \text{V}^{-1} \text{s}^{-1} \).
Values for high-purity nitrogen [41].

<table>
<thead>
<tr>
<th>( d_p ) [m]</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
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<td>4 \times 10^{-9}</td>
<td>0</td>
<td>0</td>
<td>2.89 \times 10^{-14}</td>
<td>1.32 \times 10^{-12}</td>
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<td>20 \times 10^{-9}</td>
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<td>30 \times 10^{-9}</td>
<td>2.91 \times 10^{-15}</td>
<td>6.25 \times 10^{-14}</td>
<td>5.99 \times 10^{-13}</td>
<td>4.53 \times 10^{-12}</td>
<td>2.87 \times 10^{-11}</td>
</tr>
<tr>
<td>50 \times 10^{-9}</td>
<td>3.81 \times 10^{-14}</td>
<td>2.37 \times 10^{-13}</td>
<td>1.26 \times 10^{-12}</td>
<td>5.90 \times 10^{-12}</td>
<td>2.44 \times 10^{-11}</td>
</tr>
</tbody>
</table>

\[ \alpha_{\text{coll}} = \left( \frac{r_p}{\delta} \right)^2 \] no interaction force

\[ = \left( \frac{b_{\text{min}}}{\delta} \right)^2 \] interaction force

\[ b^2 = r_{\text{aps}}^2 \left( 1 + \frac{2(\Phi(\delta) - \Phi(r_{\text{aps}}))}{3k_BT} \right) \]

\[ \Phi(l, q) = \frac{e^2}{4\pi\epsilon_0} \left( \frac{q \cdot p_{\text{ion}}}{l} - \frac{r_p^3}{2l^2(l^2 - r_p^2)} \right) \]

\( \alpha_{\text{coll}} \) is called the collision parameter, \( b_{\text{min}} \) is the minimum of \( b(r_a) \), which defines the closest distance between the particle origin and a tangent to the ion trajectory at radial distance \( \delta \). \( b_{\text{min}} \) has to be determined numerically. \( r_{\text{aps}} \) is the apsoidal distance (point of closest approach to the particle center) and used as variable in the equation above. \( \Phi(l, q) \) is the electric interaction potential between an ion and a particle from conducting material [61].

Based on this information the ion attachment coefficients can be calculated [2]:

\[ \eta_{ia}^{q-(q+1)} = \frac{4\pi r_p D_{ion}}{\overline{s}^2 c_{\text{ion}} \alpha_{\text{coll}}} \exp \frac{\Phi(l, q)}{k_BT} + \int_0^{r_p/\delta} \exp \frac{\Phi(r_p/y, q)}{k_BT} dy \] (B.3)
Appendix B. Charging

An overview of ion attachment coefficients to metallic particles is given in table B.1. Hussin et al. [124] use a slightly different formula for the attachment coefficients with the integral in the denominator evaluated. From the ion attachment coefficients the attachment rate for a fixed ion concentration is given by:

\[
\rho_{ia}^{q-q\pm 1} = n_{ia}^{q-q\pm 1} \cdot n_i \tag{B.4}
\]

The final charge distribution is calculated via the rate equations [149], which express the change of a given species (size, charge) per unit time in terms of generation and destruction rates (source and sink).

\[
\frac{d N_{q,d_p}}{d t} = \rho_{ia}^{(q-1)-q} N_{(q-1),d_p} + \rho_{ia}^{(q+1)-q} N_{(q+1),d_p} - N_{p,d_p} \left( \rho_{ia}^{q-(q+1)} + \rho_{ia}^{q-(q-1)} \right) \tag{B.5}
\]

This leads to an infinite system of coupled differential equations, which have to be solved simultaneously. Equation (B.5) holds under the assumption that the attachment rates are constant. This is true if the ion concentration remains unchanged (\(\frac{dn_{\text{ion}}}{dt} = 0\)), e.g. in case of an excess of ions. If the ion concentration also varies, two additional rate equations occur for generation/destruction of ions that couple all other equations through the charging rates. Assuming that - depending on the particle size - the maximum charge per particle is limited and the respective attachment rate is zero (\(\rho_{ia}^{q_{\text{max}}-q_{\text{max}}\pm 1} = 0\) and \(N_{q_{\text{max}}\pm 1,d_p} = 0\)) a system of \(2q_{\text{max}} + 1\) equations remain. The system can be solved for steady state conditions (\(\dot{N}_{q,d_p} = 0\)) for a monodisperse system [124, 150] (detailed derivation in appendix E):
B.1. Ion Attachment

\[ \psi^0(d_p) = \frac{N_{0,d_p}}{N(d_p)} = 1 - \sum_{q \neq 0} \frac{N_{q,d_p}}{N(d_p)} \]  \hspace{1cm} (B.6)

\[ \psi^q(d_p) = \frac{N_{q,d_p}}{N(d_p)} = \begin{cases} \frac{1}{\Pi_{q=1}^\infty (\Pi_{j=1}^{q-1} A_j \Pi_{j=1}^{q+1} A_j )} & \text{if } q > 0 \\ \frac{1}{\Pi_{q=1}^\infty (\Pi_{j=1}^{q+1} A_j \Pi_{j=1}^{q-1} A_j )} & \text{if } q < 0 \end{cases} \]  \hspace{1cm} (B.7)

\[ A_q = \begin{cases} \frac{N_q A_p}{N^{(q-1)} A_p} & \frac{\rho_i^{(q-1)q} - \rho_i^{(q+1)} - \rho_i^{(q-1)q} A_{q+1}}{\rho_i^{(q+1)} + \rho_i^{(q-1)q} A_{q-1}} \quad \text{if } q > 0 \\ \frac{N_q A_p}{N^{(q+1)} A_p} & \frac{\rho_i^{(q+1)q} - \rho_i^{(q-1)q} A_{q+1}}{\rho_i^{(q+1)} + \rho_i^{(q-1)q} A_{q-1}} \quad \text{if } q < 0 \end{cases} \]  \hspace{1cm} (B.8)

The charge distribution for a monodisperse aerosol as stated above is valid over the whole size range and accounts for different ion concentrations \( n_{ion} \) and ion properties. They are the most general solution to equations of the type (B.5). For particles smaller than \( \approx 100 \) nm a maximum charge of \( q_{max} = 2 \) can be assumed with 0.25% error. For larger particles a simpler size distribution can be derived in case of ion balance \( (n_{ion}^+ = n_{ion}^-) \) and the same ion properties for positive and negative ions [13]:

\[ N_{q,d_p} = N(d_p) \exp \left(-\frac{q^2 e^2}{d_p k T}\right) \]  \hspace{1cm} (B.9)

Equation (B.9) describes the so called Boltzmann charge distribution. However, more realistic cases include the differences in ion properties. Wiedensohler [23] fitted the charge distribution for particles between 1nm and 1000nm in diameter and a charge \(|q| \leq 2 \) in air. This approximation is used today by TSI Ltd. for many applications. An overview of ion properties used by different authors is given by Reischl et al. [148], values for high purity gases can be found at different sources [41, 52]. Alonso et al. [151] fitted the ion attachment coefficients dependent on the particle size, allowing to calculate the charge distribution for polydisperse aerosols.
Appendix B. Charging

B.2. Photoemission

Electromagnetic radiation leads to the emission of electrons, if the energy of the photons is higher or equal than the ionization energy of the particle. The emission process in vacuum is described by the 3 step model of Spicer [152], which has to be extended by a fourth step for aerosols as described by Burtscher et al. [9]:

- **Adsorption and excitation**
  Only a fraction of the photons hitting the particle is absorbed and excites an electron. The absorption probability $P_{abs}$ is calculated from Mie theory, which is a solution of Maxwell’s equations for a system of incident wave, wave propagation inside the particle and the scattered wave. The absorption efficiency is given by [4]

  $$P_{abs}(\nu) = \frac{4\pi d_p \nu}{c} \cdot \frac{\epsilon_f(\nu) - 1}{\epsilon_f(\nu) + 2}$$

  (B.10)

  The complex dielectric constant can be found listed for many materials e.g. in Landolt-Börnstein [153].

- **Escape from the surface barrier potential**
  Certain materials (some metals amongst others) can be described by the jellium-model. The atoms are represented by fixed, rigid cores with a positive charge and a negative electron “jelly” that can move rather freely around the cores. The energy of the electrons is distributed according to Fermi-Dirac statistics around the Fermi energy. Some electrons have actually left the surface, producing a negative cloud in the adjacent volume. This charge is depleted from just below the surface where a positive space charge forms. The resulting dipole layer poses a surface potential barrier, which is the electron work function. Adsorbates modify the electron density at the surface and thus have a direct influence on the electron work function. Chlorine e.g. acts as an electron donor to the surface, increasing the work function, while lithium depletes them and lowers the work function.

\[\text{For Ag at 255nm } \epsilon_a = 0.172 + 3.705i \ [153, \text{III/15B}], P(255nm) = 2.97 \cdot 10^7 d_p.\]
B.2. Photoemission

The ratio of electrons passing through the surface barrier potential per absorbed photon is called the photoyield. It follows a Fowler-Nordheim law.

$$Y^{q-(q+1)} = K_c (h \nu - \phi)^{(q+1)} b_{pe}$$

(B.11)

The exponent of photoemission $b_{pe}$ is found to be 2 for metals. The photoemission constant $K_c$ varies with particle size [8, 59, 60], chemical composition and surface state.

• Escape from image charge and photoemission potential

For small particles the energy necessary to emit an electron is increased because Coulomb forces act between the particle and the emitted electron. Additionally the electron induces an image charge in the particle. For macroscopic bodies this image charge would drift deeper into the bulk as the electron drifts away from the surface. With small particles the image charge can not move further away from the surface than the particle diameter, which increases the emission energy.

Accounting for all corrections the effective electron work function becomes [56]:

$$\phi^{q-(q+1)} = \phi_{\infty} + \frac{e^2}{4 \pi \varepsilon_0 r_p} \left( q + \frac{3}{8} \right)$$

(B.12)

Table B.2 shows absolute values of the correction of the work function due to Coulomb and image forces. Adding the bulk value of the photothreshold ($\phi_{\infty}$) yields the correct value of $\phi^{q-(q+1)}$.

Since the effective work function increases with increasing particle charge the maximum obtainable charge is limited for a given wavelength. The maximum charge is given through

$$h \nu \geq \phi^{q_{\max}-(q_{\max}+1)}$$

$$q_{\max} \leq \frac{4 \pi \varepsilon_0 r_p (h \nu - \phi_{\infty})}{e^2} - \frac{3}{8}.$$  

(B.13)
Appendix B. Charging

\[ \phi^{q+1} - \phi_{\infty} \text{ for different } q [\text{eV}] \]

<table>
<thead>
<tr>
<th>( r_p [\text{nm}] )</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.34</td>
<td>-9.00 ( \times 10^{-1} )</td>
<td>5.40 ( \times 10^{-1} )</td>
<td>1.98</td>
<td>3.42</td>
</tr>
<tr>
<td>5</td>
<td>-4.68 ( \times 10^{-1} )</td>
<td>-1.80 ( \times 10^{-1} )</td>
<td>1.08 ( \times 10^{-1} )</td>
<td>3.96 ( \times 10^{-1} )</td>
<td>6.84 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>10</td>
<td>-2.34 ( \times 10^{-1} )</td>
<td>-9.00 ( \times 10^{-2} )</td>
<td>5.40 ( \times 10^{-2} )</td>
<td>1.98 ( \times 10^{-1} )</td>
<td>3.42 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>15</td>
<td>-1.56 ( \times 10^{-1} )</td>
<td>-6.00 ( \times 10^{-2} )</td>
<td>3.60 ( \times 10^{-2} )</td>
<td>1.32 ( \times 10^{-1} )</td>
<td>2.28 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>20</td>
<td>-1.17 ( \times 10^{-1} )</td>
<td>-4.50 ( \times 10^{-2} )</td>
<td>2.70 ( \times 10^{-2} )</td>
<td>9.90 ( \times 10^{-2} )</td>
<td>1.71 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>25</td>
<td>-9.36 ( \times 10^{-2} )</td>
<td>-3.60 ( \times 10^{-2} )</td>
<td>2.16 ( \times 10^{-2} )</td>
<td>7.92 ( \times 10^{-2} )</td>
<td>1.37 ( \times 10^{-1} )</td>
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<tr>
<td>30</td>
<td>-7.80 ( \times 10^{-2} )</td>
<td>-3.00 ( \times 10^{-2} )</td>
<td>1.80 ( \times 10^{-2} )</td>
<td>6.60 ( \times 10^{-2} )</td>
<td>1.14 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>35</td>
<td>-6.68 ( \times 10^{-2} )</td>
<td>-2.57 ( \times 10^{-2} )</td>
<td>1.54 ( \times 10^{-2} )</td>
<td>5.66 ( \times 10^{-2} )</td>
<td>9.77 ( \times 10^{-2} )</td>
</tr>
</tbody>
</table>

Table B.2.: Correction to the photoelectric work function due to Coulomb forces and image charge effects on small particles

where \( q_{\text{max}} \) is nearest integer number for which the condition is fulfilled.

- **Diffusion away from the particle**
  The electron must be transported away from the particle after it has left the surface. Depending on the particle Knudsen number the mechanisms vary. The electron is caught quickly after emission by electronegative constituents of the carrier gas (either impurities or components). The ions then diffuse back to the particle surface and neutralize its charge. If the particles, however, are small as compared to the mean free path of the electron, the diffusion back to the surface is less likely and charging more efficient. According to Burtscher et al. [9] the escape probability is close to 1 for particles smaller than 100nm at a charge state lower than the maximum obtainable charge.

In analogy to ion attachment a coefficient of photoemission \((\eta^{q+1}_{pe})\) and a photoemission rate \((\rho^{q+1}_{pe})\) are defined to emphasize the symmetry between the processes.
B.3. Charging During Particle Generation

There are basically as many ways of charging as there are methods of particle generation, thus the statements made in this section are rather crude and pose by no means a complete list. However, some of the better known mechanisms will be briefly mentioned:

- **Plasma Charging**
  Plasma is defined as the state where electrons and atoms in a gaseous environment are completely separated. Many different processes such as electron-ion-recombination, chemical reactions, emission and adsorption of radiation and others occur at the same time. It is often hard to tell which process forms the determining step, e.g. whether the charge on the particles originates from a chemical reaction, photoemission, attachment of ions from the gas phase or impact ionization. However, in general processes which use a plasma to dissociate precursors often yield a large number of unipolarly charged particles. Spark discharge seems to be more in favor of ion attachment.

\[
\eta_{pe}^{q+1} = \eta_{P_{\text{abs}}}(q+1) \cdot \frac{J}{\text{Photon}}
\]

### Table B.3.

<table>
<thead>
<tr>
<th>( d_p ) [nm]</th>
<th>(-2)</th>
<th>(-1)</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4( \times 10^{-9} )</td>
<td>1.67( \times 10^{-21} )</td>
<td>5.22( \times 10^{-22} )</td>
<td>2.33( \times 10^{-24} )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10( \times 10^{-9} )</td>
<td>8.48( \times 10^{-21} )</td>
<td>4.04( \times 10^{-21} )</td>
<td>1.23( \times 10^{-21} )</td>
<td>4.35( \times 10^{-23} )</td>
<td>0</td>
</tr>
<tr>
<td>20( \times 10^{-9} )</td>
<td>3.80( \times 10^{-20} )</td>
<td>2.39( \times 10^{-20} )</td>
<td>1.31( \times 10^{-20} )</td>
<td>5.49( \times 10^{-21} )</td>
<td>1.14( \times 10^{-21} )</td>
</tr>
<tr>
<td>30( \times 10^{-9} )</td>
<td>1.01( \times 10^{-19} )</td>
<td>7.22( \times 10^{-20} )</td>
<td>4.81( \times 10^{-20} )</td>
<td>2.89( \times 10^{-20} )</td>
<td>1.46( \times 10^{-20} )</td>
</tr>
<tr>
<td>50( \times 10^{-9} )</td>
<td>2.55( \times 10^{-19} )</td>
<td>2.05( \times 10^{-19} )</td>
<td>1.60( \times 10^{-19} )</td>
<td>1.21( \times 10^{-19} )</td>
<td>8.75( \times 10^{-20} )</td>
</tr>
</tbody>
</table>

Photoemission coefficients of a metallic material with \( \varphi = 4.4eV \) and \( K_e = 4.2\cdot10^{-4}cV^{-2} \) irradiated with light of 255nm wavelength (4.86eV).

\[
\eta_{pe}^{q+1} = \frac{P_{\text{abs}} Y_{p}^{-(q+1)}}{\pi r_p^2}
\]

\[
\rho_{pe}^{q+1} = \eta_{pe}^{q+1} \cdot J_{\text{Photon}}
\]
Appendix B. Charging

and the particle charge distribution is often close to Boltzmann's distribution.

- **Friction/Contact Charging**
  When particles come in contact with a material that can act as a reservoir for charges, there is a chance of charge transfer. Practically only wall materials have to be considered since the attractive forces due to charges of opposite sign are so strong that the charged particle(s) can not separate. When the wall material is grounded the charge can dissipate and only image charge forces between the particle and the surface are present. Although these forces are still strong on scale of small particles escape is possible. A typical example for contact charging is an atomizer with following impactor (e.g. TSI model 3076).

- **Thermal Charging**
  At high temperatures the thermal energy \( k_B T \) is large enough to excite electrons beyond the ionization threshold \( \phi \). Although the attractive forces between particle and electron are strong they can diffuse apart, leaving a positive particle and a free electron, that is caught quickly by electronegative impurities in the carrier gas. The electrons in a body typically follow the Fermi-Dirac statistic. The long tail towards higher energies allows a fraction of electrons to be excited beyond the ionization threshold before actually \( k_B T = \phi \).

- **Surface Ionization**
  Hot surfaces can be used to thermally charge atoms and molecules at much lower energies as needed for thermal charging. This is one of the major charging mechanisms in evaporation/condensation techniques on metals. A much more detailed description is given in chapter 1.
Appendix C.

Data Representation and Statistics

Aerosol and particle science uses several ways to describe particle size distributions from which the log-normal particle size distribution is probably the most important one. Scientists use different notations for the same relationships and some of them are mathematically doubtful. The following chapter is meant to help understanding the different notations and define a mathematical base related to particle size distributions.

C.1. Distribution and Probability Density Functions

It is easiest to understand the use of cumulative distribution functions (CDFs) and probability density functions (PDFs) when starting out with an example:

A sample of aerosol is taken and the diameter of each individual particle is measured. The particles are then sorted by size into bins and the number is counted per bin to obtain the frequency distribution. The number of particles contained in a bin also depends on the size of the bin. If it contains all diameters obviously all particles are contained in it. If the bin is smaller it contains less particles but all bins together contain all particles again. To find out the number of particles in a given size interval \([a, b]\) the content of the bins in this size interval must be added to obtain the desired result. If \(a\) and \(b\) are not the boundaries of existing bins, miscounting occurs. To increase the resolution more and smaller bins...
can be taken until a smooth function \( \mathcal{P} \) is reached and the bins have no measurable width anymore. In mathematical terms this is the transition to infinitesimal intervals (bins with no width) and the summation is replaced by integration. When taking a larger sample containing more particles, the shape of the frequency distribution does not change, but only its height! To get comparable results, independent of the sample size, the frequency distribution function is normalized by the number of particles in the sample. This normalized function applies to all samples, independent of its size.

The normalized frequency distribution function itself represents no physically relevant data, because it is based on bins with no size. The definite integral over the interval \([a, b]\), however,

\[
\int_a^b \mathcal{P}(x)dx
\]

yields the probability of a particle having a diameter between \(a\) and \(b\). Multiplied by the total number of particles in the sample the number of particles in the size interval is obtained. This normalized function of infinitesimal small bins is called probability density function. Its definite integral represents the probability of a particle having a diameter in the interval of integration. The cumulative distribution function \(\mathcal{D}\) is defined as

\[
\mathcal{D}(x) = \int_{-\infty}^x \mathcal{P}(x')dx'
\]

Because \(\mathcal{P}\) is normalized, \(\mathcal{D}(\infty) = 1\). The cumulative distribution function multiplied by the number of particles in the sample is often called cumulative particle size distribution and measured by some instruments. If \(\mathcal{D}\) is known the definite integral of \(\mathcal{P}\) is easily calculated, because

\[
\int_a^b \mathcal{P}(x)dx = \mathcal{D}(b) - \mathcal{D}(a).
\]

Three different parameters can be used to describe the position of a size distribution on the x axis:

- The count mean diameter
C.2. The Normal Distribution

The count mean diameter is the count weighted average diameter:

\[ \bar{x} = \frac{\sum n x}{N} \]

with \( n \) being the number of particles with size \( x \) and \( N \) being the total number of particles.

- **The count median diameter**
  It cuts the number of particles in half, thus the same number of particles are smaller as they are larger than this diameter. The cumulative distribution function at the count median diameter has the value 0.5. It is the position parameter for normal distributions.

- **The count mode diameter**
  It represents the diameter with the highest particle frequency, thus the peak position.

C.2. The Normal Distribution

The normal or Gaussian distribution describes many natural processes. It is symmetric around the mean diameter and mode, mean and median diameters are at the same position. The PDF is given by

\[ p(x) = \frac{1}{2\pi \sigma} \exp \left( -\frac{(x - \mu)^2}{2\sigma^2} \right) \]

with \( \sigma \) being the standard deviation and \( \mu \) being the count median diameter of the distribution. The standard deviation is a measure of the width of the distribution function. The interval from \([\mu - \sigma, \mu + \sigma]\) contains 68% of the particles, the interval \([\mu - 2\sigma, \mu + 2\sigma]\) contains 95.4%, the interval \([\mu - 3\sigma, \mu + 3\sigma]\) contains 99.7%.

The cumulative density function of the normal distribution is called error function and often abbreviated \( erf \) on computersystems. There is no analytical solution, but its values are tabulated.
Appendix C. Data Representation and Statistics

C.3. The log-normal Distribution

The log-normal distribution is probably the most frequently used size distribution in aerosol technology, because it describes a distribution obtained from coagulation processes (self preserving log-normal size distribution, e.g. [13, 119]). It represents a process where the logarithm of the variable (the diameter) has a normal distribution. It can be obtained by substituting $x$ and $\mu$ with their respective natural logarithms. One obtains

$$P_n(x) \, dx = \frac{1}{2\pi \sigma} \exp \left( \frac{-(\ln(x) - \ln(\mu))^2}{2\sigma^2} \right) \, dx$$

The differential $dx$ has to be transformed as well, if the function is still plotted vs. the diameter. When plotting the particle size distribution vs. the natural logarithm of $x$ one obtains a normal distribution. The parameter $\mu$ in the log-normal distribution still represents the count mean diameter ($50\%$ count), but mode and median diameter are not the same anymore. They are calculated via:

$$d = \mu \exp(b \ln^2(\sigma))$$

with $b = -1$ for the mode diameter and $b = 0.5$ for the count mean diameter [119, 154].

C.4. Representation

Size distributions can be presented in different ways. Dependent on the abscissa of the plot the variable in the PDF must be transformed. Figure C.1 shows the same size distribution plotted vs. different values on the abscissa.

It is necessary to change the units on the ordinate according to the units on the abscissa. As stated above the integral of the PDF yields the respective particle concentration, not the PDF itself. Thereby it does not matter, whether the distance between the size values is on logarithmic
C.4. Representation

Figure C.1.: Size distribution plotted vs. particle size (left) and logarithm of particle size (right). The respective PDFs were used (log-normal left, normal right).

or linear scale! The same is valid for the plot vs. the logarithm of the particle diameter. Since the logarithm has no units\footnote{Actually the particle diameter must be normalized with 1m before taking the logarithm. Since this does not change the numeric value it often is done intuitively by dropping the unit.} the units of the PDF change accordingly. They are the same as the desired measurement value since the value of the PDF does not represent particle concentration. The integral over a certain interval must be calculated to obtain it.

The respective function is transformed as well. The log-normal PDF was plotted vs. the diameter, while the normal PDF was plotted vs. the logarithm of the diameter. Thereby the position of the mode changes. Often $dN/d\log(D_p)$ is plotted vs. $D_p$ on logarithmic abscissa. In this case the normal, not the log-normal PDF is plotted. This representation is misleading, because the apparent mode size of the (normal) distribution is not the real mode size, which occurs at smaller particle sizes. However, this is easily checked by analyzing the units.
C.5. Diameter Definitions

In aerosol technology a number of different diameters is used to describe particles depending on the measurement method and measured properties.

- **The Stokes diameter** $d_s$
  is defined via the settling velocity of a particle and is defined as "the diameter of a sphere that has the same density and settling velocity as the particle" in question [119].

- **The aerodynamic diameter** $d_a$
  is defined as the diameter of a water droplet with the same aerodynamic properties as the particle in question.

- **The mass equivalent diameter** $d_m$
  is defined as the diameter of a sphere with the same mass as the particle in question.

- **The volume equivalent diameter** $d_V$
  is defined as the diameter of a sphere with the same volume as the particle in question.

- **The mobility equivalent diameter** $d_p$
  is defined as the diameter of a particle with the same aerodynamic mobility as the particle in question.

Stokes, aerodynamic and mass equivalent diameter are often used when inertial processes are considered, while the volume and mobility equivalent diameter are used to describe particles moving along with the gas stream. The mobility equivalent diameter is obtained from DMA measurements. Due to deviation from bulk density and spherical shape actual particle size obtained from microscopy and size obtained from aerosol measurements can differ strongly. There is no simple relationship between shape and aerosol diameters so measurements have to be analyzed carefully before comparison.

The diameters are connected via the following relationships:
C.5. Diameter Definitions

\[ v_s = B(d_p) \rho_p g \frac{1}{6} \pi d_s^3 = B(d_p) g \frac{1}{6} \pi d_s^3 \]  
(C.1)

\[ m_p = \frac{1}{6} \pi d_m^3 \]  
(C.2)

\[ B = \frac{C_c(d_p)}{3 \pi \eta d_p} \]  
(C.3)

The mechanical mobility \( B \) and Cunningham slip correction are defined in chapter A.
Appendix D.

Units

Today the Système international d’unités (SI-System) is the system of units and measures used in science. It is based on the decisions of the General Conference on Weights and Measures (Conférence Générale des Poids et Mesures, CGPM) formed by 51 member states and 20 associates (as of 10/2005, Bureau International Des Poids et Mesures, BIPM [155]). The SI-System is based on 7 base units and units derived from them, although some SI base units (mol, Ampere, candela) can even be expressed in terms of the other units. The standard is currently (2006) defined in ISO1000:1992 and NEN1000:1993. A further description can be found in the brochure "The International Systems of Units (SI)” [156]. Table D.1 shows a selection of the base units and the derived units with special names.

Some of the older but important papers on aerosol technology [e.g. 2] are written at a time where the cgs-system was widely used. The relation between the two systems is especially in electromagnetism not only by means of multiples of 10. Often factors containing $\pi, c$ or $\epsilon_0$ occur. In order to facilitate the transition from one system to the other table D.2 gives an overview for some commonly used properties.
### Appendix D. Units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Base Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>Meter*</td>
<td>m</td>
</tr>
<tr>
<td>Mass</td>
<td>Kilogram*</td>
<td>kg</td>
</tr>
<tr>
<td>Time</td>
<td>Second*</td>
<td>s</td>
</tr>
<tr>
<td>Temperature</td>
<td>Kelvin*</td>
<td>K</td>
</tr>
<tr>
<td>Amount of substance</td>
<td>Mol*</td>
<td>mol</td>
</tr>
<tr>
<td>Luminous intensity</td>
<td>Candela [cd]*</td>
<td>$\frac{W}{sr}$</td>
</tr>
<tr>
<td>Current</td>
<td>Ampere [A]*</td>
<td>$(\sqrt{\frac{cd}{sr}}, \text{ESU})$</td>
</tr>
<tr>
<td>Frequency</td>
<td>Hertz [Hz]</td>
<td>$s^{-1}$</td>
</tr>
<tr>
<td>Force</td>
<td>Newton [N]</td>
<td>$\frac{kg \cdot m}{s^2}$</td>
</tr>
<tr>
<td>Energy/Work</td>
<td>Joule [J]</td>
<td>$\frac{kg \cdot m^2}{s^2}$</td>
</tr>
<tr>
<td>Power</td>
<td>Watt [W]</td>
<td>$\frac{kg \cdot m^2}{s^3}$</td>
</tr>
<tr>
<td>Pressure</td>
<td>Pascal [Pa]</td>
<td>$\frac{kg}{m \cdot s}$</td>
</tr>
<tr>
<td>Charge</td>
<td>Coulomb [C]</td>
<td>As</td>
</tr>
<tr>
<td>Electric Potential</td>
<td>Volt [V]</td>
<td>$\frac{kg \cdot m^2}{A \cdot s}$</td>
</tr>
<tr>
<td>Resistance</td>
<td>Ohm [$\Omega$]</td>
<td>$\frac{kg \cdot m^2}{A \cdot s^2}$</td>
</tr>
<tr>
<td>Conductance</td>
<td>Siemens [S]</td>
<td>$\frac{A \cdot s}{kg \cdot m^2}$</td>
</tr>
<tr>
<td>Inductance</td>
<td>Henry [H]</td>
<td>$\frac{kg \cdot m^2}{A^2 \cdot s}$</td>
</tr>
<tr>
<td>Capacitance</td>
<td>Farad [F]</td>
<td>$\frac{A^2 \cdot s}{kg \cdot m^2}$</td>
</tr>
<tr>
<td>Magnetic Flux</td>
<td>Weber [Wb]</td>
<td>$\frac{kg \cdot m^2}{A^2 \cdot s}$</td>
</tr>
<tr>
<td>Magnetic Flux Density</td>
<td>Tesla [T]</td>
<td>$\frac{kg}{A^2 \cdot s}$</td>
</tr>
</tbody>
</table>

Table D.1.: 
SI base units (starred) and a selection of derived units with a special name [156]
<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>SI to cgs</th>
<th>cgs to SI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>$I$</td>
<td>$\sqrt{4\pi \varepsilon_0} \cdot I$</td>
<td>$\frac{i}{\sqrt{4\pi \varepsilon_0}}$</td>
</tr>
<tr>
<td>Charge</td>
<td>$Q$</td>
<td>$\sqrt{4\pi \varepsilon_0} \cdot Q$</td>
<td>$\frac{q}{\sqrt{4\pi \varepsilon_0}}$</td>
</tr>
<tr>
<td>Electric potential</td>
<td>$\Phi$</td>
<td>$\frac{\Phi}{\sqrt{4\pi \varepsilon_0}}$</td>
<td>$\sqrt{4\pi \varepsilon_0} \cdot \Phi$</td>
</tr>
<tr>
<td>Electric field strength</td>
<td>$E$</td>
<td>$\frac{E}{\sqrt{4\pi \varepsilon_0}}$</td>
<td>$\sqrt{4\pi \varepsilon_0} \cdot E$</td>
</tr>
<tr>
<td>Resistance</td>
<td>$R$</td>
<td>$\frac{R}{4\pi \varepsilon_0}$</td>
<td>$4\pi \varepsilon_0 \cdot R$</td>
</tr>
</tbody>
</table>

Table D.2:
Conversions between SI and cgs equations. The respective symbol has to be replaced by the expression listed in the table for conversion.
Appendix E.

Derivations

E.1. Charging

Equation (B.8) can be derived from equation (B.5) for constant $d_p$ as follows:\footnote{Subscripts $d_p$ and $ia$ are dropped.}

$$\frac{d N_{q_{dp}}}{dt} = \rho_{ia}^{(q-1)\rightarrow q} N_{q-1_{dp}} + \rho_{ia}^{(q+1)\rightarrow q} N_{q+1_{dp}}$$

$$N_{q_{dp}}^{\text{source}} - N_{q_{dp}}^{\text{sink}} \left( \rho_{ia}^{q\rightarrow (q+1)} + \rho_{ia}^{q\rightarrow (q-1)} \right) \quad (B.5)$$

Steady state:

$$\frac{d N_{q}}{dt} = 0$$

$$0 = \rho^{(q-1)\rightarrow q} N_{q-1} + \rho^{(q+1)\rightarrow q} N_{q+1} - N_{q} \left( \rho^{q\rightarrow (q+1)} + \rho^{q\rightarrow (q-1)} \right)$$

Divide by $N$ to get to probabilities:

$$\frac{N_{q}}{N} = \psi^{q},$$
Appendix E. Derivations

then

\[ 0 = \rho^{(q-1)\to q} \psi^{(q-1)} + \rho^{(q+1)\to q} \psi^{(q+1)} - \psi^q \left( \rho^{(q+1)\to q} + \rho^{q\to (q-1)} \right), \]

divide by \( \psi^q \)

\[
\left( \rho^{(q+1)\to q} + \rho^{q\to (q-1)} \right) = \rho^{(q-1)\to q} \frac{\psi^{(q-1)}}{\psi^q} + \rho^{(q+1)\to q} \frac{\psi^{(q+1)}}{\psi^q}
\]

and solve to:

\[
A_q = \frac{\psi^q}{\psi^{(q-1)}} = \frac{\rho^{(q-1)\to q}}{\rho^{q\to (q-1)} + \rho^{(q+1)\to q} A_{(q+1)}} \quad \text{if } q > 0
\]

\[
A_q = \frac{\psi^q}{\psi^{(q+1)}} = \frac{\rho^{q\to (q-1)}}{\rho^{q\to (q-1)} + \rho^{(q+1)\to q} A_{(q-1)}} \quad \text{if } q < 0
\]

The probability ratios are recursively defined. Assuming, that there is a maximum charge and the respective charging rate to that state becomes zero, \(2q_{\text{max}}\) coefficients exist.

It is obvious, that:

\[
\prod_{j=1}^{q} A_j = \frac{\psi^1}{\psi^0} \cdot \frac{\psi^2}{\psi^1} \cdot \ldots \cdot \frac{\psi^{(q-1)}}{\psi^{(q-2)}} \cdot \frac{\psi^q}{\psi^{(q-1)}} = \psi^q \quad \text{if } q > 0
\]

\[
\prod_{j=-q}^{-1} A_j = \frac{\psi^{-1}}{\psi^0} \cdot \frac{\psi^{-2}}{\psi^{-1}} \cdot \ldots \cdot \frac{\psi^{(1-q)}}{\psi^{(2-q)}} \cdot \frac{\psi^{-q}}{\psi^{(1-q)}} = \psi^{-q} \quad \text{if } q < 0
\]

Thus writing out equation (B.7)

\[
\psi^q = \frac{\prod_{j=1}^{q} A_j}{\left(1 + \sum_{j=1}^{\infty} \left(\prod_{j=1}^{j} A_j + \prod_{j=-j}^{-1} A_j\right)\right)} \quad \text{(B.7)}
\]
yields

\[
\psi_q = \frac{\psi_q}{\psi_0} = \left( 1 + \sum_{i=1}^{\infty} \left( \frac{\psi_i}{\psi_0} + \frac{\psi_{-i}}{\psi_0} \right) \right) = \left( \psi_0 + \sum_{i=1}^{\infty} \left( \psi_i + \psi_{-i} \right) \right).
\]

Per definition

\[
\sum_i \psi_i = 1,
\]

hence

\[
\psi_q = \psi_q.
\]

Multiplying with \(N\) yields

\[
N\psi_q = N \cdot \psi_q = \psi_0 + \sum_{i=1}^{\infty} \psi_i + \psi_{-i}
\]

\[
\left( N_0 + \sum_{i=1}^{\infty} N_i + N_{-i} \right) \cdot \psi_q = N \psi_q,
\]

and

\[
N_0 = N - \sum_{i=1}^{\infty} N_i + N_{-i} = N - \sum_{i \neq 0} N_i.
\]

Equation (B.7) contains all information that is needed for the solution of a finite system of differential equations of type (B.5), thus with limited \(q\) and constant rate factors.
Appendix F.

Parameters of Simulation

**General Parameters**

- $c \cdot \nu^{-1} = 254 \cdot 10^{-9}$ wavelength of light [m]
- $J_{\text{photon}} = 8.34 \cdot 10^{18}$ photon flux density [m$^{-2}$ s$^{-2}$]
- $D_{\text{ion}} = 2.15 \cdot 10^{-4}$ diffusion coefficient ions [m$^2$ s$^{-1}$]
- $T = 293.15$ ambient temperature [K]
- $p = 1.013 \cdot 10^5$ ambient pressure [Pa]
- $\delta_g = 3.7 \cdot 10^{-16}$ scattering diameter of the ambient gas [m]
- $m_{\text{gas}} = 4.831 \cdot 10^{-26}$ molecular mass of sheath gas [kg]

**DMA Data**

- $L_{\text{DMA}} = 203.3 \cdot 10^{-3}$ DMA-length [m]
- $r_i = 9 \cdot 10^{-3}$ DMA inner radius [m]
- $r_o = 19 \cdot 10^{-3}$ DMA outer radius [m]
- $\Delta S = 1 \cdot 10^{-3}$ Width of DMA exit slit [m]
- $Q_{\text{sheath}} = 2.3$ DMA sheath air flow [l min$^{-1}$]

**Particle type 1**

- $N_{c,M} = 5000$ Number of particles in sample volume
- $K_c = 4.2 \cdot 10^{-4}$ Constant for Fowler-Nordheim Law [eV$^{-2}$]
- $\varphi_{\infty} = 4.4$ Bulk work function [eV]
- $r_p = 11 \cdot 10^{-9}$ Primary particle diameter [m]
- $q = 1$ Particle charge

**Particle type 2**

- $N_{c,M} = 5000$ Number of particles in sample volume
- $K_c = 4.2 \cdot 10^{-4}$ Constant for Fowler-Nordheim Law [eV$^{-2}$]
- $\varphi_{\infty} = 4.4$ Bulk work function [eV]
- $r_p = 11 \cdot 10^{-9}$ Primary particle diameter [m]
- $q = 1$ Particle charge
Bibliography


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            Delft University of Technology