

Chapter 1: Introduction

1.1. Introduction and Background

Science is immersed in a period of investigating objects with dimensions on the nanoscale, including nanometer thick films (quantum wells), nanorods, nanotubes, nanowires, and nanoparticles. These objects often have optical,[1] magnetic,[2] and/or catalytic[3] properties that are different from micron-scale materials due to the quantum confinement effect. The smallest of these objects is the nanoparticle, and it can serve as the active component of a system[4] or can be used in the synthesis of nanorods,[5] nanotubes,[6] and nanowires.[7] The flexibility of nanoparticles increases its potential as a building block in future, more-complex structures.

Nanoparticles have been synthesized in many different ways, including using liquid and gas-phase techniques. For liquid techniques, each new particle composition requires a new optimization procedure of the synthesis parameters (i.e., precursor, concentration, surfactant, temperature, solvent) to obtain a narrow particle size distribution for the desired application. This process is inefficient if a small quantity of nanoparticles is desired for a particular application.

Gas-phase synthesis is preferred due to the continuous nature of particle production and the ease of manipulating aerosol particles. The classic reactor for nanoparticle production is the Sinclair–La Mer generator[8] that creates nanoparticles through the thermal decomposition of a precursor in a furnace at high temperatures. The reactor volume required to achieve high temperatures leads to long residence times, causing the particles to agglomerate and a broadening of the particle size distribution. A

narrower distribution of particles was obtained through using mixing jets to dilute the nanoparticles before agglomeration occurred.[9] Yet, a major obstacle for these systems is that the reactor walls tend to become coated with decomposed precursor and nanoparticles eventually fouling the reactor to the point that nanoparticle synthesis is no longer viable.

A microplasma is a simple, generic synthesis route for small quantities of nanoparticles of many chemical compositions.[10] Synthesis involves passing a gaseous precursor through the microplasma, where it decomposes and forms nanoparticles. The short residence time provides an intense reaction zone to produce nanoparticles. The microplasma operates steadily for hours, producing stable particle size distributions. The particle size distribution was measured *in situ* using a Radial Differential Mobility Analyzer (RDMA).

The combination of the microplasma and the RDMA was a solid initial platform on which to build, but was incapable of measuring these small particles without significant distortion of the size distribution. The microplasma produced particles in the 1 to 5 nm size range, and the RDMA was optimized for particle size measurements in the 8 to 100 nm size range.[11] The lower size limit of the RDMA is due to diffusion that causes measured size distributions to appear broader than they actually are. The breadth of a size distribution is an important indicator of the growth process. Broad distributions tend to result when growth occurs due to agglomeration whereas narrow distributions are the result of homogeneous nucleation.

The approach taken in this dissertation was to construct a new RDMA (i.e., the nano-RDMA) capable of measuring particle size as small as 1 nm, believed to be

produced in the microplasma. Before presenting any results on this combination, a brief background will be given on the individual topics.

1.2. Plasma Background

Plasma is a state of matter that consists of ions, electrons, and neutrals where the ionized species represent a significant percentage of the overall number density (i.e., 0.01% to 10%).[12] The large number density of the ions and electrons leads to the plasma volume being conductive and causes the plasma to exhibit collective dynamics with the presence of each species (i.e., ions and electrons) causing fields and influencing the motion of the other species.

Plasma operation is strongly influenced by the number density of neutrals, which is directly related to the system pressure. The microplasma used throughout this dissertation is a direct current microhollow cathode discharge (MHCD) that operates at atmospheric pressure. Sustaining a plasma at atmospheric pressure is quite difficult due to the numerous collisions between the ions and electrons that will quench the plasma.

The geometry of the MHCD facilitates this process. The MHCD consists of two electrodes with the cathode biased negatively with respect to the anode that are placed a fixed distance apart. The cathode is the crucial electrode and is cylindrical in nature with a characteristic radius on the order of 100 μm to decrease the electric field required to initiate the discharge. Inside the cathode, the high-energy electrons are created, and correspondingly the most intense plasma exists here.

The plasma glow extends from the inner volume of the cathode to the anode. The conductive nature of the plasma results in a small voltage drop across the plasma volume. Without the MHCD, the electric field is mainly in the axial direction, but with the

MHCD, the electric field becomes radial in direction with a strong electric field developing between the electrode and the plasma. The radial electric field confines the electrons inside the cathode and causes them to oscillate in a manner known as the Pendel effect.[13]

The second impact of the number of collisions at atmospheric pressure is collision-induced heating. Ions are accelerated and collide with neutral gas molecules transferring energy to the background gas molecules. The collisions increase the neutral gas temperature.

The combination of joule heating and high-energy electrons facilitate the decomposition of gas molecules in the MHCD. Decomposed gaseous precursor may lead to a local supersaturation of growth species that cluster and form nanoparticles. These become naturally charged due to the electrons and ions in the discharge and emerge as an aerosol.

1.3. Aerosol Mobility Measurements Background

An aerosol consists of a suspension of fine particles dispersed in a gas. The behavior of the particles is dependent upon and characterized by a number of factors. The most critical parameters for the studies considered herein are particle concentration, size, and size range. The goals of this section will be to discuss the topics of aerosol research relevant to this work, to give a brief overview of how these topics are related, and to indicate reasoning behind decisions made about equipment and analysis. The concepts discussed in this section will be utilized extensively in the following chapters without further explanation.

1.3.1. Particle Size

The relevant physics of particle motion are determined by the number and type of interactions with the background gas molecules. The dimensionless group that accounts for these interactions is the Knudsen number (Kn), defined as

$$Kn = \frac{2\lambda}{D_p}, \quad (1.1)$$

where λ is the mean free path of the background gas molecules and D_p is the mobility diameter of the particle. Small values of Kn (i.e., $Kn \ll 1$) correspond to the continuum limit, a regime in which particle motion is impeded due to collisions with the background gas. The mobility of a particle (B) in this regime is defined by the well-known Stokes-Einstein relationship:

$$B = \frac{1}{3\pi\mu D_p}, \quad (1.2)$$

where μ is the viscosity. The mobility relationship is different when the value of Kn nears unity (i.e., the transition regime). An empirical factor (the Stokes–Cunningham slip correction factor $C_c(Kn)$), [14] is introduced to account for the apparent slippage of gas molecules past the surface of the particle. The mobility relationship becomes

$$B = \frac{C_c(Kn)}{3\pi\mu D_p}. \quad (1.3)$$

This relationship holds for all values of Kn . The slip correction factor is directly proportional to Kn at large values of Kn . The mobility becomes proportional to the inverse of the diameter squared, indicating that smaller particles are more mobile due to decreased resistance to motion. The inverse squared dependence on diameter is the same that is observed for particle mobility in the free-molecular limit, which is

$$B = 0.441 \frac{(k_B T / m)^{0.5}}{p D_p^2}, \quad (1.4)$$

where k_B is the Boltzmann constant, T is the temperature, m is the mass of the background gas molecule, and p is the pressure. Given that the value of λ at standard conditions is approximately 60 nm and the particle diameters considered in this report are 10 nm and smaller, the transition regime expression will be utilized to convert particle mobility to mobility diameter.

The particle mobility diameter assumes that the particle is spherical. Formulas to account for different particle shapes can be applied,[15] but the particles measured in this report were not expected to be aspherical. The particle mobility diameter is not equivalent to the particle diameter, and the error in assuming so becomes important as the size approaches molecular and atomic dimensions. Tammet recognized the difference could be corrected with a simple formula:

$$d = D_p - d_g, \quad (1.5)$$

where d is the actual diameter of the particle and d_g is a correction related to the finite diameter of the background gas.[16] The value of d_g has been calculated from a few sources to be approximately 0.55 nm.[17]

The previous mobility expressions have been presented in terms of resistance to particle motion. The motion of the particle can be due to a variety of sources, including thermal energy (diffusivity) and electrical potential energy (electrophoretic mobility), resulting in the following mobility expressions:

$$D = B * k_B T; \quad (1.6)$$

$$Z_p = B * i q, \quad (1.7)$$

where D is the diffusivity, Z_p is the electrophoretic mobility, i is the number of elementary charges on a particle and q is the fundamental unit of charge (i.e., $1.602 * 10^{-19}$ coulombs). Diffusion causes an isotropic motion of the particle whereas electrophoretic motion is a directional process that depends on the electric field, E . The directionality can be exploited to classify aerosol nanoparticles according to their electrophoretic mobility due to differences in mobility diameter. The standard aerosol equipment to perform this separation is the differential mobility analyzer (DMA). A more complete description of the DMA will be provided in chapter 2.

1.3.2. Particle Concentration

Particle concentration is measured typically with two devices: a condensation particle counter (CPC) and a faraday cup electrometer (FCE). The CPC is primarily used for detection of low particle concentrations. CPC operation is based on measuring scattered light intensity from particles that have been enlarged through condensing a working fluid on the surface of the particle. It can be used to detect both neutral and charged particles, and the presence of multiple charges does not influence the detected concentration. The detector is ideal for many applications except those involving small particle sizes (<2.5 nm), as small particles can not be overgrown to larger sizes and therefore cannot be detected. Considerable research is currently underway to overcome this size limit.[18]

The FCE is used primarily for detection of high concentrations of charged particles found largely in nanoparticle synthesis systems. It detects particles through the current generated by charged particles that are collected on filter cartridges. No lower size limit exists for the FCE as the filtration efficiency improves as particle size

decreases. The limit on FCE operation is that detected currents must be greater than ± 1 fA, as the Johnson noise of the high impedance resistor in the detection circuit impedes detection below approximately 0.5 fA.[19] For the experiments described herein, the particle sizes detected were below the lower size limit of available CPCs and the measured concentrations were high ($\gg 1$ fA). Therefore, the FCE was the primary particle detection instrument.

1.3.3. Log-Normal Distribution

The total particle concentration and particle size can be measured independently, but significant information is gained about the system when measured together. The combination of size and concentration naturally lends itself toward analysis with a distribution function. For aerosol applications, the appropriate function is the log-normal distribution:[20]

$$f(D_p, N, D_{pg}, \sigma_g) = \frac{N}{(2\pi)^{0.5} \ln \sigma_g} \exp\left(-\frac{1}{2} \left(\frac{\ln D_p - \ln D_{pg}}{\ln \sigma_g}\right)^2\right) \quad (1.8)$$

where D_p is the mobility diameter, N is the concentration, D_{pg} is the geometric mean mobility diameter, and σ_g is the geometric standard deviation. The geometric standard deviation indicates the range of particle sizes. Its value provides important insight on the dynamics of the aerosol such as the importance of agglomeration.

1.3.4. Agglomeration

Agglomeration is the result of two particles colliding and sticking together, resulting in a physically larger particle (i.e., increases D_{pg} and σ_g) and a net loss of one

particle (i.e., decreases N). The agglomeration process between two particles (i and j) has been described theoretically as a rate ($J_{i,j}$), using the following equation:[14]

$$J_{i,j} = K_{i,j} N_i N_j, \quad (1.9)$$

where $K_{i,j}$ is the agglomeration coefficient and N_i is the concentration of particles with size i . The coefficient $K_{i,j}$ has many different forms, but generally depends on the diameters of the particles involved in the collision. Interestingly, $K_{i,j}$ is minimized when $i = j$, as particles with the same size will have the same mobility. These particles will move at the same rate, resulting in a average relative rate of motion that is smaller than if the particles were not the same size. This implies that monodisperse distributions will remain monodisperse longer than polydisperse aerosols of the same concentration. As the agglomeration process naturally creates a polydisperse aerosol, the distribution will continue to broaden (i.e., larger σ_g) with time until a self-preserving distribution (at t_{spd}) is reached that is characterized by a $\sigma_g > 1.3$. The particle concentration will decrease rapidly past t_{spd} . [14]

The particle size and concentration are the most important parameters in determining the amount of time before agglomeration will impact the measured size of the distribution. High concentration (N) and polydisperse (larger σ_g) aerosols will decrease the onset time for the effects of agglomeration. The effects of agglomeration can be overcome through reducing the number concentration and narrowing the size distribution, as is accomplished in the Tandem DMA (TDMA) arrangement (discussed further in chapters 8 and 9).

1.4. Dissertation Outline

The remaining chapters chronicle a majority of the work that has been completed. Chapter 2 will present work associated with the design, construction, and testing of the new differential mobility analyzer (i.e., the nano-RDMA). It will include instrument calibration results found using molecular ions, and work completed in collaboration with others. The mass spectroscopy work to confirm the identity of the molecular ion was completed with Evan Neiholdt in the lab of Professor J. L. Beauchamp. The comparison of the nano-RDMA to other DMAs was completed with Dr. Jingkun Jiang and Professor M. Attoui in the lab of Professor P. McMurry. Chapter 3 will present finite element simulations used to characterize the ideal operation of the nano-RDMA, and will include some recommended improvements to the nano-RDMA construction.

The remaining chapters will report work completed with the combination of the microplasma and the nano-RDMA. Chapter 4 will present some work completed to characterize the production of nanoparticles with the microplasma that was improved due to the use of the nano-RDMA. Particles were observed for lower precursor concentration than previously reported (i.e., <3 ppm) as well as without precursor due to cathode sputtering. The size distribution of particles produced from cathode sputtering are presented in chapter 5. The flexibility of the microplasma is demonstrated in chapter 6, where narrow size distributions of iron nanoparticles were synthesized. The iron nanoparticles were shown to produce similarly narrow distributions of carbon nanotubes. The growth of carbon nanotubes was completed in collaboration with Professor J. Kim.

Chapter 7 will discuss the microplasma as a particle source to calibrate the nano-RDMA in the Tandem DMA (TDMA) arrangement. The ability of the TDMA

arrangement will be demonstrated in chapter 8, where the size evolution of silicon nanoparticles is monitored as a function of the thermal processing temperature. While chapter 8 demonstrates the size reduction of silicon nanoparticles, chapter 9 will discuss the methods used to grow silicon nanoparticles to larger sizes.

Finally, some ideas for future work will be presented in chapter 10 before the electro spray sources created (appendix I) and some collaborative work completed with other students will be described (appendix II with Áron Varga and appendix III with Dean Holunga).

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