UNIVERSITY OF CAMBRIDGE

Robert Nishida
PhD Candidate

Supervisor: Prof. Simone Hochgreb
Adviser: Dr. Adam Boies,
(Aerosol Society Committee Member)

C N Davies Award Application Essay

Aerosol nanoparticles are more efficiently charged by direct ultraviolet (UV) photoionization than by other charging mechanisms such as corona discharge, particularly for particle sizes less than 50 nm diameter. The higher charging efficiency provides an opportunity for better detection, capture, and control of aerosol nanoparticles. However, photoionization and charge recombination processes are not well characterized. Mechanisms of particle charge recombination with gaseous ions are well understood, but models often neglect particle and ion wall losses and flow geometry effects.

In my PhD research, I use the photoionization process as illustrated in Fig. 1, along with detection electronics, to determine the size and concentration of aerosol nanoparticles. The results of my research will be commercialized in an environmental or personal exposure monitoring device. In this essay, I frame my research in terms of the project motivation and background and I argue my suitability to execute the project.

I am continuing to conduct experiments to investigate the behaviour of UV particle charging and subsequent charge transport and collection in a continuous flow as a means for quantitative detection and classification of particles. I have developed a comprehensive computational fluid dynamics (CFD) model and have shown that simulations agree well with experimental results. My initial results confirm the feasibility of a measurement device based on UV photoionization and I am pursuing further investigations.

Motivation

Combustion and other industrial processes generate airborne particulate matter which creates smog and causes negative health effects. Inhalable nanoparticles, particles under 300 nanometers in diameter, can be particularly harmful as they can penetrate the alveoli of the lungs and transport into the bloodstream [1]. These particles are more biologically active as they have larger surface area per mass than larger particles of the same material. These particles account for more than 90% of airborne particles and reach concentrations of 10^4-10^5 cm^{-3} in urban areas [2].

Air quality monitoring is crucial to regulate and control air pollution in urban areas and industrial workplaces and it requires accurate and traceable quantification of pollutants. Conventional light-scattering methods are not effective for measurement due to the small sizes of particles under consideration. Existing methods for detection of nanoparticles are often costly (>£10K), require full bench-top systems or are accurate only in idealized conditions. A network of low-cost, distributable sensors for inhalable particles could be used in

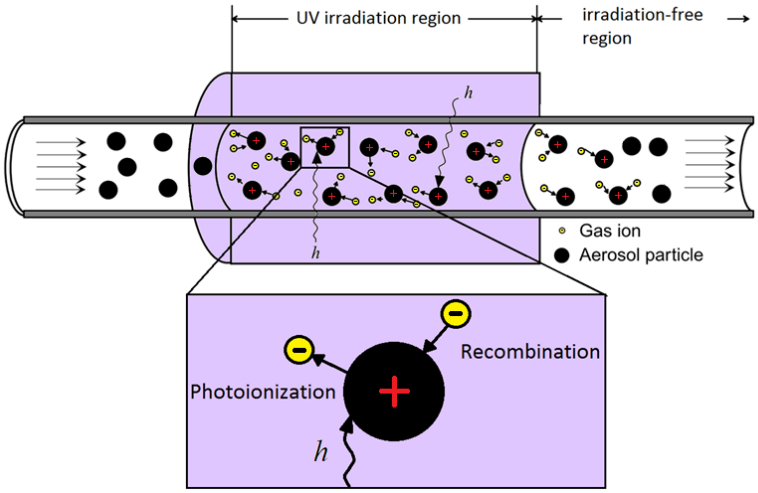

Figure 1: Photionization and recombination of particles entrained in flow. UV photons are absorbed causing the particles to emit electrons which in turn form gaseous ions. The gaseous ions may diffuse back to and recombine with the charged particles, thereby neutralizing them.

urban areas or transport centres to carry out source attribution, inform policy and provide information for epidemiological studies [3]. Other applications of such sensors include personal exposure monitoring, workplace hazard and exposure identification, filtration efficiency verification, and engine and vehicle emissions monitoring.

Background Information

Aerosol nanoparticles are often classified by aerodynamic diameter, particle mass or electrical mobility in a range of configurations which yield information on size and concentration independent of chemistry. Measurement devices commonly charge, classify and count aerosol particles entrained in flow. Devices range in quality of particle information, accuracy and cost.

Conventional Nanoparticle Measurement Systems

A Scanning Mobility Particle Size Spectrometer (SMPS) is regarded as a standard measurement system to classify aerosol particles [4]. It combines an impactor, neutralizer, Differential Mobility Analyzer (DMA) and a Condensation Particle Counter (CPC). The impactor directs high velocity, polydisperse flow towards a flat impactor plate to collect only the largest particles which would interfere with measurements. The charging section is generally a neutralizer which first ionizes gas molecules with a radioactive ^{85}Kr source. The ions transfer charge to the particles due to diffusive and attractive electrical forces resulting in a known bipolar charge distribution of positive, negative and neutral particles which is independent of ion concentration [5, 6]. In the DMA, the charged particles flow between two concentric electrodes. When an electric field is applied, particles of one polarity move towards a slit at

the end of the DMA to be counted by the CPC. By varying the electric field and flow rate, only particles of a known electric mobility will be counted thereby yielding a distribution of particle sizes. The CPC uses the nanoparticles as nucleation sites for condensing a substance such as butanol into droplets to be counted by optical methods. The CPC counts the concentration of particles, but cannot distinguish particle size when operating alone. The SMPS controls for multiply charged particles with a transfer function corresponding to the well known Fuch's charge distribution [7].

Other measurement systems include the Electrical Low Pressure Impactor (ELPI) which measures aerodynamic diameter in a cascade of impactor stages after electric charging [8]. The Aerodynamic Aerosol Classifier (AAC) balances aerodynamic and centrifugal forces without the need for electrical charging [9]. Particle mass can be measured directly, for example, by a Centrifugal Particle Mass Analyzer (CPMA) which balances electrostatic and centrifugal forces [10, 11].

The conventional aerosol measurement systems can yield high quality information for a wide range of particle sizes and types. However the devices require large, bench-top systems, high power, long sampling times, complex flow control, high maintenance and even radioactive or X-ray ion chargers. More recently, smaller, lower cost and portable alternatives which operate on similar principles to conventional methods have gained interest for particle measurements.

Low-cost Nanoparticle Sensors

Compact, low-cost nanoparticle sensors for field measurements combine charging, classification and detection into smaller, sometimes handheld, devices (DiSCmini, Naneos Partector, NSAM, NanoTracer). The devices each use corona discharge to generate ions which subsequently transfer charge to particles. Then, charged particles are captured and sensed via currents on the order of 10 fA with highly sensitive electrometers. Each of the devices measures lung deposited surface area (LDSA), or the fraction of airborne particle surface area concentration that would deposit in a human lung. The instruments measure particles with approximately the size dependence of the particle surface area weighted with the alveolar or tracheobronchial deposition curve: $D_{p,av}$ [12] for the NanoTracer, $D_p^{1.13}$ for the NSAM [13], and $D_p^{1.1}$ [14] for the Naneos Partector and DiSCmini. Therefore, LDSA can be derived by multiplying total current with a calibration factor [15]. The NanoTracer and DiSCmini give an additional estimate of size and concentration. The NanoTracer operates a low-efficiency electrostatic precipitator which alternately captures smaller particles with a square wave voltage yielding two signals. In the DiSCmini, there two consecutive filter stages in which particles are preferentially deposited based on size. In both devices, two signals are used to derive mean particle size and concentration assuming a lognormal distribution [15].

A field measurement device based on photoelectric charging is commercially available (PAS 2200CE). The device uses a UV lamp to ionize particles rather than by diffusion charging. Excess ions are captured in an ion trap and the remaining positively charged particles are collected on a filter inside and electrometer. The output measurement is a

current which can be used with site-specific calibration to give a measure of aerosol carbon content depending on the application.

Sensor Charging Methods

In all of the low-cost devices and most of the conventional systems, it is necessary to electrically charge the particles for classification or detection. The advantage of bipolar charging techniques such as radioactive, soft X-ray and bipolar corona discharge ionization is that a well defined equilibrium of charge can be established [16]. The charge efficiency is limited which reduces signal strength, but also reduces unwanted multiply charged particles. Unipolar charging methods such as corona discharge achieve higher charging efficiencies, but introduce more multiply charged particles which must be considered. Corona discharge is used in fast mobility analyzers (Models: EEPS, FMPS, DMS500) where parallel measurement requires an efficient charging technique. Corona discharge is used in portable sensors as radioactive and X-ray sources are not suitable for field measurements.

Corona chargers are generally reliable and charging depends weakly on material. However, they require high voltage power converters (on the order of 3 kV), always produce some ozone and, depending on the carrier gas, undesired species or particles may result [17]. Charging efficiency of corona based chargers is a function of the ion-to-particle attachment coefficient which causes low efficiency charging particularly for particles less than 50 nm in diameter. Multiple charging effects are higher than in bipolar charging techniques, but are limited due to Coulomb repulsion forces [18].

Direct particle photoionization using ultraviolet (UV) light charges particles with much higher efficiency than diffusion based methods for a range of particle sizes. Photoionization of nanoparticles can occur without producing ozone and without the need for high voltage sources. However, the process is material dependent and design considerations such as photoemission from housing walls must be considered [19].

Proposed Research

Small, low-cost field sensors are required for regulation and control of nanoparticle emissions among other applications. As health effects are better understood, measurements of the smallest particles are becoming more valuable. Conventional measurement methods are prohibitively expensive, immobile, or do not adequately sense particles less than 50 nm diameter, thereby sacrificing accuracy. Aerosol nanoparticles are more efficiently charged by direct UV photoionization than by other charging mechanisms such as corona discharge. The higher charging efficiency presents an opportunity for better detection of aerosol nanoparticle size and concentration in an environmental or personal exposure monitoring device. However, the material dependent response, which has hindered previous commercial success, must be addressed.

The processes involved in nanoparticle photoionization are not well characterized for different particle types or larger sizes into the accumulation mode. Existing models include empirical constants which vary for particle size and type. Mechanisms of particle charge

recombination with gaseous ions are well understood, but models often neglect particle and ion wall losses and flow geometry effects. In this work, comprehensive theoretical, modelling and experimental techniques are developed to investigate photoionization, particle/ion interactions and transport. Developments in understanding are used to inform design decisions towards a method for quantitative classification and detection of particles.

Scope

The aim of my research is to understand the fundamental photoionization mechanisms, particle/ion interactions and transport of nanoparticles from the free molecular to continuum regimes in order to refine a detection method for nanoparticle size and concentration in an aerosol flow. To accomplish this, I have analysed theoretical equations, applied them in a computational fluid dynamics model and compared them with experimental results for validation.

The computational fluid dynamics (CFD) model I developed is the first to include equations capturing UV photoionization and detailed ion/particle recombination theory. In addition, the model solves ion/particle advection and diffusion, wall losses and electric field transport in three-dimensional CFD. Upwards of fifty simultaneous species transport equations are solved to allow the resolution of local charge distribution and average charges per particle for multiple charge states. The computational domain reflects the geometry of the experimental set-up created in-house, however, the method allows full user control to inexpensively test changes in geometry or operating parameters. Results from the CFD model are verified by comparing with those from published 1-D models which are further replicated in MATLAB [20, 21]. I am in the process of writing up a journal article which will describe the modelling advances and address the limitations of previous models.

I have conducted preliminary experiments to assess two operating methods for a proposed environmental sensor using a controlled nanoparticle source, prototype sensor and aerosol instrumentation. I compared experimental results with those from the CFD model for a range of operating parameters to begin validation of the model and theoretical equations. The results demonstrate the feasibility of the proposed operating methods, the limitations of previous models and areas for design improvements. A patent agent is currently writing a patent for the proposed operating methods.

Throughout the rest of my PhD studies, I will develop further advancements in the CFD model and theoretical understanding, re-design the prototype sensor adding instrumentation, and further test the accuracy of the sensor in a range of conditions. Along with the core goals of my research, I will pursue the benefits of aerosol nanoparticle charging on the fabrication of novel catalyst structures, as well as explore the possibility of capturing photoionized particles for air filtration.

About the applicant

Throughout my PhD project, I will address fundamental research questions while I develop techniques, tools, and designs for energy and climate-related technologies. My proven

abilities in academics, research, and leadership make me an ideal candidate for the C N Davies research award.

During my five year undergraduate degree at the Institute for Energy Systems at the University of Victoria, I completed four years of academic study, five four-month co-op work terms, and a minor in business. I maintained a high GPA and graduated with distinction. It was there I developed my desire to research alternative energy systems.

This desire led me to the Queens-RMC Fuel Cell Research Centre at Queen's University where I studied solid oxide fuel cells as a graduate fellowship holder with first class academic standing. For my Master's thesis research, I developed a computational fluid dynamics models to study the detailed interactions between flow geometry, fluid dynamics, and electrochemical reactions in solid oxide fuel cell stacks. During that time I gained a deep understanding of a complex multi-physics research problem while developing strong self-discipline and work ethic.

My extra-curricular experiences have greatly enhanced my education. I served as the elected Council Representative for the Department of Mechanical and Materials Engineering on the Society of Graduate and Professional Students (SGPS) Council for a two year term during my Master's degree program. In that capacity, I provided support services to the student body and advocated for them when debating policy and budget decisions. I also served as the elected Graduate Student Representative on the Faculty of Engineering and Applied Science Graduate Council for the 2012-2013 academic year. I gained valuable experience discussing matters such as changes to graduate degree program and course requirements. I offered thoughtful ideas and conveyed them clearly in communication with faculty. I have continued my involvement in student government as Treasurer for the Clare Hall College Graduate Student Body. I represent the students' voice on College Finance Committee and manage an annual budget of £6500. For the past five years, I have volunteered at science outreach events (Science Rendezvous in Kingston, Canada, and Cambridge Science Festival) where I have performed science demonstrations to engage budding young scientists from the community. Through these types of experiences, I was able to practise my leadership, teamwork, and communication skills.

My academic achievements are an indicator of the level of performance I strive to achieve in my research and extracurricular activities. I have a proven record of contributing valuable research and, given the opportunity, will represent well the student members of Aerosol Society. Please consider me for a C N Davies Research Award.

References

[1] Günter Oberdörster, Eva Oberdörster, and Jan Oberdörster. Review Nanotoxicology : An Emerging Discipline Evolving from Studies of Ultrafine Particles. 113(7):823–839, 2005.

[2] Beverly S Cohen. Health effects of ambient ultrafine particles. pages 205–216, 2005.

[3] M.I. Mead, O.a.M. Popoola, G.B. Stewart, P. Landshoff, M. Calleja, M. Hayes, J.J.

Baldovi, M.W. McLeod, T.F. Hodgson, J. Dicks, a. Lewis, J. Cohen, R. Baron, J.R. Saffell, and R.L. Jones. The use of electrochemical sensors for monitoring urban air quality in low-cost, high-density networks. *Atmospheric Environment*, 70:186–203, 2013.

[4] Shih Chen Wang and Richard C. Flagan. Scanning Electrical Mobility Spectrometer. *Aerosol Science and Technology*, 13(November):230–240, 1990.

[5] N. A. Fuchs. On the stationary charge distribution on aerosol particles in a bipolar ionic atmosphere. *Geofisica Pura e Applicata*, 56(2):185–193, 1963.

[6] A. Wiedensohler. An approximation of the bipolar charge distribution for particles in the submicron size range. *Journal of Aerosol Science*, 19(1):387–389, 1988.

[7] W.A. Hoppel. Determination of the aerosol size distribution from the mobility distribution of the charged fraction of aerosols. *Journal of Aerosol Science*, 9:41–54, 1978.

[8] Marko Marjama, Jorma Keskinen, Da-ren Chen, and David Y H Pui. Performance evaluation of the electrical low-pressure impactor (ELPI). 31(2), 2000.

[9] Farzan Tavakoli, Jonathan P. R. Symonds, and Jason S. Olfert. Generation of a Monodisperse Size-Classified Aerosol Independent of Particle Charge. *Aerosol Science and Technology*, 48(3):i–iv, 2014.

[10] J. S. Olfert and N. Collings. New method for particle mass classification - The Couette centrifugal particle mass analyzer. *Journal of Aerosol Science*, 36:1338–1352, 2005.

[11] Kensei Ehara, Charles Hagwood, and Kevin J. Coakley. Novel method to classify aerosol particles according to their mass-to-charge ratioAerosol particle mass analyser. *Journal of Aerosol Science*, 27(2):217–234, 1996.

[12] Johan Marra, Matthias Voetz, and H. J. Kiesling. Monitor for detecting and assessing exposure to airborne nanoparticles. *Journal of Nanoparticle Research*, 12:21–37, 2010.

[13] Heejung Jung and David B. Kittelson. Characterization of Aerosol Surface Instruments in Transition Regime. *Aerosol Science and Technology*, 39:902–911, 2005.

[14] M. Fierz, C. Houle, P. Steigmeier, and H. Burtscher. Design, Calibration, and Field Performance of a Miniature Diffusion Size Classifier. *Aerosol Science and Technology*, 45(November):1–10, 2011.

[15] Christof Asbach, Heinz Kaminski, Daniel Von Barany, Thomas a J Kuhlbusch, Christian Monz, Nico Dziurowitz, Johannes Pelzer, Katja Vossen, Knut Berlin, Silvio Dietrich, Uwe Götz, Heinz Jürgen Kiesling, Rudolf Schierl, and Dirk Dahmann. Comparability of portable nanoparticle exposure monitors. *Annals of Occupational Hygiene*, 56(5):606–621, 2012.

[16] Peter Kallinger, Gerhard Steiner, and Wladyslaw W. Szymanski. Characterization of four different bipolar charging devices for nanoparticle charge conditioning. *Journal of Nanoparticle Research*, 14:944, 2012.

[17] B. Grob, H. Burtscher, and R. Niessner. Charging of Ultra-fine Aerosol Particles by an Ozone-Free Indirect UV Photo-Charger. *Aerosol Science and Technology*, (January 2014):130909190419001, 2013.

[18] Lin Li and Da Ren Chen. Aerosol charging using pen-type UV lamps. *Aerosol and Air Quality Research*, 11(1992):791–801, 2011.

[19] D. Matter, M. Mohr, W. Fendel, a. Schmidt-Ott, and H. Burtscher. Multiple wavelength aerosol photoemission by excimer lamps. *Journal of Aerosol Science*, 26(7):1101–1115, 1995.

[20] Arkadi Maisels, Frank Jordan, and Heinz Fissan. Dynamics of the aerosol particle photocharging process. *Journal of Applied Physics*, 91(2002):3377–3383, 2002.

[21] Arkadi Maisels, Frank Jordan, and Heinz Fissan. On the effect of charge recombination on the aerosol charge distribution in photocharging systems. *Journal of Aerosol Science*, 34:117–132, 2003.