

# **Particle Charging and Classification: The Mass Mobility Aerosol Spectrometer (M<sup>2</sup>AS)**



**Joshua Savio Hassim**

Department of Engineering  
University of Cambridge

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I dedicate this thesis to my parents, Berni and Conan, and my girlfriend, Ali; without you, I would not have been able to complete this journey.



## **Declaration**

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the preface and specified in the text. It is not substantially the same as any work that has already been submitted, or is being concurrently submitted, for any degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the preface and specified in the text. It does not exceed the prescribed word limit for the relevant Degree Committee.

Joshua Savio Hassim

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## Abstract

Quantifying aerosols is essential for understanding their behaviour and assessing their impacts on health, the environment, and industrial applications. Accurate characterisation plays a critical role in evaluating air quality and respiratory health risks, optimising manufacturing processes, and improving climate models. Many aerosol quantification methods rely on particle charging and classification techniques, where particles are charged and classified based on their electrical mobility or mass-to-charge ratio. Diffusion charging is commonly used to impart a known charge to particles, enabling precise classification through instruments such as differential mobility analysers (DMAs) and particle mass analysers (PMAs). These methods provide detailed insights into particle size, mass, and morphology, all of which are crucial for understanding aerosol dynamics and enhancing measurement accuracy across various applications.

While the effects of humidity on aerosol behaviour are well-recognised, their influence on particle charging has received limited attention, particularly in the context of charging sensors. In this work, the effect of humidity on particle charging behaviour is investigated, as it is a critical but often overlooked parameter in ambient measurement contexts. It is demonstrated that the ions produced by particle chargers are directly influenced by the presence of water vapour, which, depending on the charging technique, can significantly alter the charging process. This underscores the importance of accounting for humidity effects when interpreting data from charging-based measurement devices, ensuring more accurate and reliable results.

Next, the operation of unipolar charger-classifier systems is investigated, specifically the pairing of a unipolar diffusion charger with a Centrifugal Particle Mass Analyser (CPMA). Theoretical models for multiple charge correction in these systems are first experimentally verified, enabling the determination of the average transmitted particle mass. This method proves effective for a wide range of aerosols (mass range of 0.01 fg to 100 fg) and achieves accuracy within  $\pm 20\%$  by fitting experimental data to power law functions of mobility diameter for both effective density and average charge. This experimental study highlights a key challenge in unipolar charger-CPMA systems: the inherent uncertainty in relating aerosol mass, charge, and mobility.

To address this challenge, the Mobility Separator Electrometer (MSE) is introduced, a new classifier designed to measure average charge and average particle electrical mobility when combined with a condensation particle counter (CPC). The MSE enhances the performance of unipolar charger-classifier systems. The MSE's transfer function is validated through numerical and experimental studies. Its integration with existing classification systems, such as the CPMA and the Aerodynamic Aerosol Classifier (AAC), is also examined. The influence of particle morphology and system operating conditions on measurements is investigated, further improving classification accuracy. The experimental validation of an AAC-MSE-CPC system using compact aerosols demonstrates good agreement with bulk density measurements, showcasing the system's accuracy.

The MSE's ability to precisely measure particle charge and mobility significantly enhances the accuracy of unipolar charger-classifier systems. However, challenges remain in accurately measuring particle mass distributions using PMAs due to uncertainties in the relationships between mass, mobility, and charge. A numerical investigation is performed into the determination of number-weighted mass distributions using a unipolar charger-PMA system. It is demonstrated that this approach requires assumptions about particle charge and mobility, which, if incorrect, can introduce errors in the measured mass distribution. Building on the enhanced classification accuracy provided by the MSE, the Mass Mobility Aerosol Spectrometer ( $M^2AS$ ) is introduced. This novel system improves measurement accuracy by incorporating the MSE as a particle classifier. By measuring the average charge and electrical mobility downstream of the CPMA, the  $M^2AS$  system refines the calculation of the system transfer function, reducing sensitivity to variations in measurement conditions and further advancing aerosol mass characterisation.

The final part of this work is the experimental validation of the  $M^2AS$  system. The  $M^2AS$  demonstrated good agreement of effective density measurements for DOS and ammonium sulphate, with accuracy within 8.2% for particles smaller than 1  $\mu m$ , but performed worse for larger particle sizes. Distribution validation of the same aerosols showed good consistency with SMPS measurements, with discrepancies within 10% for geometric mean diameter and standard deviation. However, large overestimations (up to a factor of 2) in total concentration were observed, particularly for smaller particles. Additionally, the system's measurements of the mass-mobility pre-factor and exponent of non-spherical soot particles were within 10% of CPMA-SMPS results. However, the mobility distribution of  $M^2AS$  measurements was systematically larger and narrower than the corresponding SMPS distribution. One of the suggested reasons for this systematic disagreement was confirmed by preliminary comparisons with two-dimensional inversion of CPMA-SMPS data, which revealed skew in the effective density measurements, corroborating previously introduced numerical models.

These results underscore the potential of the M<sup>2</sup>AS for precise aerosol characterisation, with further improvements needed to address the identified challenges.



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# Nomenclature

## Greek Symbols

$\alpha$  Ion Recombination Coefficient  $\text{m}^3 \text{s}^{-1}$

$\alpha_c, \beta_c, \gamma_c$  Cunningham Slip Constants

$\alpha_\omega, \beta_\omega$  Parameters used to describe CPMA angular velocity profile,  $\text{s}^{-1}$ ,  $\text{m}^2 \text{s}^{-1}$

$\beta$  Aerosol to Sheath flow ratio, Inverse of Resolution or Ion-Aerosol Attachment Coefficient

$\chi$  Dynamic Shape Factor

$\Delta$  Difference

$\delta$  Limiting Sphere Radius, m

$\varepsilon$  Particle Conductivity, error term

$\varepsilon_0$  Permittivity of Free Space,  $8.85 \times 10^{-12} \text{m}^{-3} \text{kg}^{-1} \text{s}^4 \text{A}^2$

$\eta$  Counting Efficiency of CPC

$\kappa$  Material Dielectric Constant

$\lambda_\Lambda, \lambda_\mu$  Area and width scaling factors of AAC transfer function

$\lambda_{\text{DMA}}$  HRDMA Penetration Factor

$\mu$  Air Viscosity,  $\text{kg m}^{-1} \text{s}^{-1}$

$\nu$  Average Charge Power Law Exponent

$\Omega, \Lambda$  Non-dimensional transfer function of classifier

$\omega$  Rotational Speed,  $\text{rad s}^{-1}$

---

|                                    |                                                                |
|------------------------------------|----------------------------------------------------------------|
| $\overline{\sigma}_{\text{ph}}$    | Photoelectrically Active Surface Area                          |
| $\Phi$                             | Electric Flux Function, V m                                    |
| $\phi$                             | Potential, V                                                   |
| $\Psi$                             | Stream Function, $\text{m}^3 \text{s}^{-1}$                    |
| $\rho_0$                           | Unit Density, $1000 \text{ kg m}^{-3}$                         |
| $\rho_{\text{eff},100}/\rho_{100}$ | Effective Density of a 100 nm particle, $\text{kg m}^{-3}$     |
| $\rho_{\text{eff}}$                | Effective Density, $\text{kg m}^{-3}$                          |
| $\sigma$                           | Diffusive Spreading Parameter/Standard Deviation, m            |
| $\sigma_{d_m}$                     | Geometric Standard Deviation of mobility diameter distribution |
| $\sigma_{m d_m}$                   | Geometric Standard Deviation of conditional mass distribution  |
| $\sigma_m$                         | Geometric Standard Deviation of mass distribution              |
| $\tau$                             | Relaxation Time, s                                             |
| $\tau^*$                           | Relaxation Time set-point of AAC, s                            |

### Roman Symbols

|                       |                                                                                      |
|-----------------------|--------------------------------------------------------------------------------------|
| <b><math>A</math></b> | Matrix of discretised Kernel                                                         |
| <b><math>N</math></b> | Vector of Concentration Measurements                                                 |
| <b><math>p</math></b> | Vector of additional quantities required to describe an instrument transfer function |
| <b><math>x</math></b> | Vector of discretised distribution                                                   |
| $\lambda$             | Mean Free Path, m                                                                    |
| $\overline{c}_i$      | Mean Ion Speed, $\text{m s}^{-1}$                                                    |
| $\overline{q}$        | Average charge                                                                       |
| $\overline{U}$        | Average Flow Velocity, $\text{m s}^{-1}$                                             |
| $\overline{Z}_p$      | Average Electrical Mobility, $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$                |
| $\rho_p$              | Material Density, $\text{kg m}^{-3}$                                                 |

$a, b, c$  Generic Constants

$B$  Mechanical Mobility,  $\text{m s}^{-2}$

$C_3, C_4$  Coefficients of Taylor series expansions for the particle migration velocity in CPMA

$C_c()$  Cunningham Slip Correction Factor

$C_c$  Cunningham Slip Correction Factor

$D$  Diffusion Coefficient,  $\text{m}^2 \text{s}^{-1}$

$d$  Particle Diameter, m

$d_a$  Particle Aerodynamic Diameter, m

$d_g$  Geometric mean diameter of mobility diameter distribution, m

$D_m$  Effective Density Exponent

$d_m$  Particle Mobility Diameter, m

$d_{ve}$  Volume Equivalent Diameter, m

$e$  electron charge,  $1.602 \times 10^{-19} \text{ C}$

$E_r, E_x$  Radial and axial electric field,  $\text{V m}^{-1}$

$f()$  Probability Density Function

$F$  Force, N

$F_C$  Centrifugal Force, N

$F_D$  Drag Force, N

$F_E$  Electrostatic Force, N

$f_q()$  Particle Charge Distribution Function

$G_o(r)$  Operator to map particle trajectory in CPMA, m

$h\nu$  Specific Photon Energy, eV

$I$  Irradiation Intensity,  $\text{W m}^{-2}$

$i$  Current, A

---

|                   |                                                                   |
|-------------------|-------------------------------------------------------------------|
| $K()$             | Kernel                                                            |
| $k$               | Effective Density Pre-factor, non-physical units                  |
| $k_b$             | Boltzmann Constant, $1.380\,649 \times 10^{-23} \text{ J K}^{-1}$ |
| $K_E$             | Coulomb's Constant, $9 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$  |
| $L$               | Classifier Length, m                                              |
| $m$               | Particle mass, kg                                                 |
| $m_g d_m$         | Geometric mean mass conditional on a given mobility diameter, kg  |
| $m_g$             | Geometric mean mass, kg                                           |
| $n(x)$            | Number distribution of some quantity $x$ , $\text{cm}^{-3}$       |
| $n$               | INTAC Interpolation Factor                                        |
| $n_i$             | Ion Concentration, $\text{m}^{-3}$                                |
| $N_{\text{tot}}$  | Number Concentration, $\text{cm}^{-3}$                            |
| $P$               | Pressure, Pa                                                      |
| $P_{\text{tube}}$ | Tube Penetration                                                  |
| $q$               | Number of elementary charges                                      |
| $q_0$             | Average Charge Power Law Pre-factor                               |
| $Q_a$             | Aerosol/Sample flow rate, $\text{m}^3 \text{ s}^{-1}$             |
| $Q_{sh}$          | Sheath flow rate, $\text{m}^3 \text{ s}^{-1}$                     |
| $r$               | Radial coordinate, m                                              |
| $r_1$             | Inner Radius, m                                                   |
| $r_2$             | Outer Radius, m                                                   |
| $r_c$             | Classifier mid-point radius, m                                    |
| $R_m$             | Mass Resolution Parameter of CPMA                                 |
| $R_{m,+1}$        | Single Charge Mass Resolution Parameter of CPMA                   |

---

|            |                                                                             |
|------------|-----------------------------------------------------------------------------|
| $R_{m,q}$  | Unipolarly Charged Mass Resolution Parameter of CPMA                        |
| $S$        | Sutherland Constant, 110.4 K                                                |
| $s^*$      | Mass-to-charge set-point of CPMA, kg                                        |
| $T$        | Temperature, K                                                              |
| $t$        | Time, s                                                                     |
| $u$        | Uncertainty                                                                 |
| $u_r, u_x$ | Radial and axial flow velocity, $\text{m s}^{-1}$                           |
| $V$        | Classifier Voltage, V                                                       |
| $V_T$      | Terminal Velocity $\text{m s}^{-1}$                                         |
| $x$        | Axial coordinate or Generic Variable, m                                     |
| $Y$        | Quantum Yield Per Incident Photon                                           |
| $Z^*$      | DMA Electrical Mobility Set-point, $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ |
| $Z_+$      | Positive Ion Mobility, $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$             |
| $Z_-$      | Negative Ion Mobility, $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$             |
| $Z_p$      | Electrical Mobility, $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$               |

### Subscripts and Superscripts

|     |                                                                                        |
|-----|----------------------------------------------------------------------------------------|
| *   | Classifier Set-point                                                                   |
| 0   | Denotes neutral fraction or reference value                                            |
| -   | Denotes average property                                                               |
| /   | Denotes a limiting particle characteristic in relation to transfer function resolution |
| max | Maximum                                                                                |
| $c$ | Property evaluated at centre of classifier                                             |
| $i$ | Denotes $i^{\text{th}}$ measurement point or ion property                              |
| $q$ | Particle Charge State                                                                  |



# Acronyms

**<sup>85</sup>Kr** Krypton-85 Isotope.

**AAC** Aerodynamic Aerosol Classifier.

**APM** Aerosol Particle Mass Analyser.

**APS** Aerodynamic Particle Sizer.

**AS** Ammonium Sulphate.

**CERMS** CPMA Electrometer Reference Mass Standard.

**CFD** Computational Fluid Dynamics.

**CMD** Count Median Diameter.

**CPC** Condensation Particle Counter.

**CPMA** Centrifugal Particle Mass Analyser.

**DMA** Differential Mobility Analyser.

**DMS** Differential Mobility Spectrometer.

**DOS** Di-octyl Sebacate.

**ELPI** Electrical Low Pressure Impactor.

**ESP** Electrostatic Precipitator.

**GMD** Geometric Mean Diameter.

**GSD** Geometric Standard Deviation.

**HEPA** High Efficiency Particulate Air (filter).

**HRDMA** High Resolution Differential Mobility Analyser.

**INTAC** Interpolated Average Charge Algorithm.

**M<sup>2</sup>AS** Mass Mobility Aerosol Spectrometer.

**MFM** Mass Flow Meter.

**MOUDI** Microorifice Uniform Deposit Impactor.

**MSE** Mobility Separator Electrometer.

**NaCl** Sodium Chloride.

**PAH** Polycyclic Aromatic Hydrocarbons.

**PLAC** Power Law Average Charge Algorithm.

**PM<sub>2.5</sub>** Particle Matter.

**PMA** Particle Mass Analyser.

**PPMV** Parts Per Million On a Volume Basis.

**PSL** Polystyrene Latex Sphere.

**QCM** Quartz Crystal Microbalance.

**RH** Relative Humidity.

**SMPS** Scanning Mobility Particle Sizer.

**SP2** Single Particle Soot Photometer.

**UDAC** Unipolar Diffusion Aerosol Charger.

**UV** Ultra-violet.





# Chapter 1

## Introduction

### 1.1 Motivation

Aerosols are defined as solid or liquid particles suspended in a gas [70]. These particles can originate from a variety of sources, both natural—such as fog, mist, or dust—and anthropogenic, including combustion processes, pesticide spraying, and the abrasion of vehicle brakes and tyres. Aerosols are also intentionally generated in industrial applications, such as in the production of powders, spray-dried products, battery materials, and drug formulations. In these cases, the production process must be meticulously controlled to achieve specific aerosol properties, which can only be done through accurate measurement and quantification.

One of the most pressing concerns surrounding aerosols is their impact on human health, particularly in relation to local air pollution. Extensive research has demonstrated the harmful effects of fine particulate matter (PM<sub>2.5</sub>) and ultrafine particles ( $d \leq 100$  nm), which are known to contribute to various cardiopulmonary diseases and premature mortality [105, 92]. In fact, millions of premature deaths each year are attributed to exposure to these airborne particles [8]. This has led to growing efforts to regulate particulate emissions from their sources [52, 54]. Effective regulations, however, require a deep understanding of aerosol characteristics and the precise methods needed to measure and quantify them.

High-precision aerosol measurement systems are capable of resolving the full particle size distribution, a fundamental characteristic of polydisperse aerosols. Since aerosol particles are often irregular in shape, direct measurement of their physical dimensions can be challenging. To address this, various equivalent diameters are used to characterise particle size. For example, the mobility diameter is defined as the diameter of a spherical particle with the same electrical mobility as the particle being measured. Whereas, the aerodynamic diameter corresponds to the diameter of a unit-density sphere that has the same settling velocity as

the particle. These equivalent diameters provide standardised metrics that relate to different physical or dynamical properties of particles, allowing comparison and interpretation across studies despite irregular particle shapes. Significant progress has been made in methods for measuring these diameters [211, 79], yet there remains a notable gap in techniques for quantifying the full mass distribution of aerosols [99]. Mass is a particularly valuable metric because, unlike particle diameters, it is independent of particle shape and surrounding gas conditions. However, relying on a single property—whether mobility diameter, aerodynamic diameter, or mass—fails to fully characterise an aerosol. Such measurements overlook key morphological features, which can strongly influence particle transport, toxicity, and the behaviour of engineered nanomaterials [42, 11, 205, 60, 23]. A comprehensive approach to aerosol characterisation must therefore incorporate morphology alongside size and mass.

In contrast, portable and low-cost sensors (LCS) are designed to provide integrated measurements, often reporting number or mass concentration. These instruments offer ease of use and accessibility, but typically report only average metrics, limiting their ability to resolve the full spectrum of aerosol properties. Charging-based LCS present an advantage over optical sensors, as they are capable of detecting smaller particles, including those below 300 nm [141, 136, 173]. However, while optical sensors have been widely tested under varying environmental conditions, particularly changes in relative humidity [38, 39, 210], charging sensors have not been subject to the same level of investigation. With the growing use of portable instruments, it is essential to assess how their performance is affected by environmental factors such as temperature, pressure [15, 16], and relative humidity [38].

## **1.2 Measurement of aerosol properties; average properties, size distributions and morphology**

### **1.2.1 Measurement techniques for aerosol quantification**

Aerosol measurements can be broadly separated into two categories as illustrated in Figure 1.1. The first, depicted in Figure 1.1a, are high-resolution aerosol size measurement systems in which resolved particle size distributions are measured. An aerosol is often conditioned by a charger, classified through the balance of forces on the particle in continuous flow and then counted by a particle counter. Depending on the classification method used, the charger may not be required. The classification method determines the measurement property of the aerosol, which can be changed by altering the forces induced on the aerosol. This is discussed further in the subsequent sections. The second measurements are low-cost systems, depicted in Figure 1.1b, which are typically more applicable for environmental and

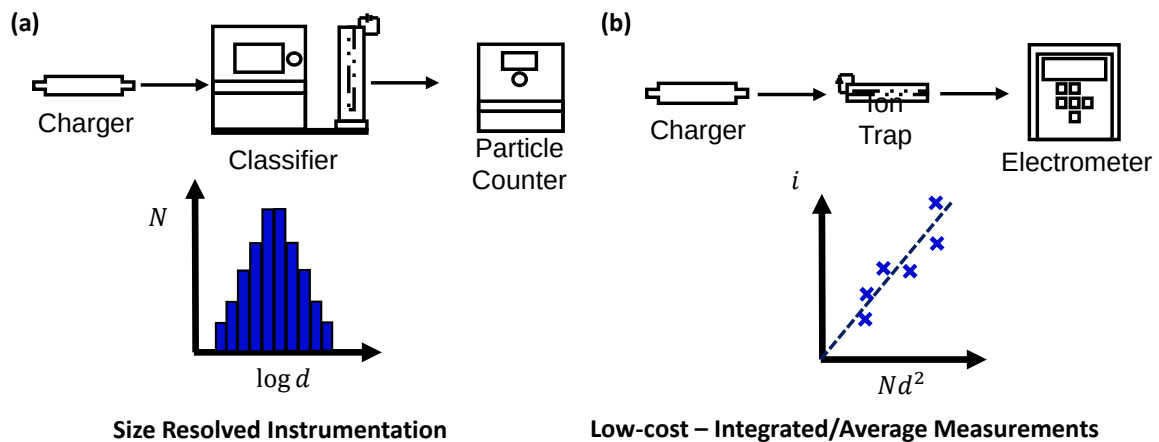


Fig. 1.1 Schematic demonstrating typical aerosol measurements which can broadly be separated into (a) resolved high-cost, laboratory-grade measurements and (b) low-cost portable charging-based measurements which provide measurements of integrated aerosol distribution parameters

exposure monitoring. Within these devices, the aerosol is still charged, but the classification stage is forgone, and the counter is replaced with an electrometer, which measures the total current attributed to the charged aerosol. The integrated current can be related to a distribution quantity such as total number concentration or total surface area, often referred to as moments of the particle size distribution [70]. In the case of both systems, accurate knowledge of how the system responds to different factors, which might include the prevailing ambient conditions, particle shape, and particle charge, is required. If each system is not well understood, greater uncertainty is introduced into the conclusions drawn from the measurements.

It should be noted that optical particle counters provide alternative methods for measuring particles; however, they are generally better suited to particles in the super-micron size range. Their effectiveness diminishes when measuring smaller particles, particularly in the sub-micron range, where scattering signals become weaker and more difficult to interpret reliably. In contrast, the instrumentation shown in Figure 1.1 can measure particles down to sizes as low as 10 nm. For this reason, optical particle counters are omitted from the discussion in this context.

### 1.2.2 Aerosol Classifiers

Aerosol classifiers are the cornerstone of obtaining highly resolved particle size distribution measurements (*e.g.* Figure 1.2) and are heavily used within this thesis; as such, their operation

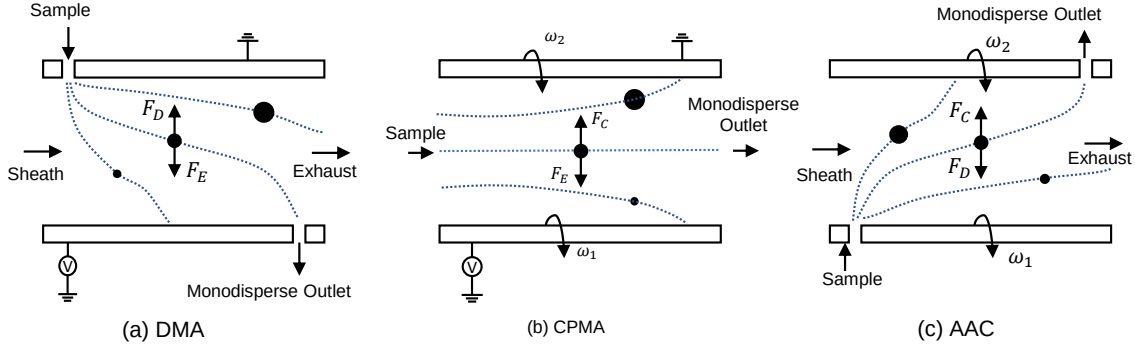


Fig. 1.2 Schematics of three aerosol classifiers (a) DMA, (b) CPMA, (c) AAC illustrating sample, sheath and outlet flow locations and example particle trajectories including the forces experienced by particles within the classifier.

and applications are described within this section. Aerosol classification typically involves balancing two opposing forces on an aerosol such that a subset of particles of a given property from a population can be selected and subsequently measured. The three classifiers used within this thesis are the Differential Mobility Analyser (DMA), Aerodynamic Aerosol Classifier (AAC) and Centrifugal Particle Mass Analyser (CPMA). Figure 1.2 illustrates a schematic of each classifier, indicating example particle trajectories.

The Differential Mobility Analyser is the most common instrument used to measure particle mobility. Illustrated in Figure 1.2 a, the DMA was first demonstrated by Knutson and Whitby [98]. A DMA classifies particles by their drag-to-charge ratio, more commonly referred to as electrical mobility,  $Z_p$ . A potential difference is applied between the inner and outer cylinder, which induces an electrostatic force ( $F_E$ ) on a particle proportional to its charge. This force results in radial migration of the particle, which is counteracted by a drag force ( $F_D$ ). The axial movement of the particle is dictated by the total volumetric flow rate through the classifier. The selected particle electrical mobility can be changed by varying the applied voltage,  $V$  and sheath flow rate  $Q_{sh}$ . For a cylindrical DMA, operating with balanced flows, the electrical mobility of particles at the monodisperse outlet is given by [98]

$$Z_p^* = \frac{-Q_{sh} \ln(\frac{r_2}{r_1})}{2\pi LV} \quad (1.01)$$

where  $L$  is the length of the classifier and  $r_1$  and  $r_2$  are the inner and outer radii respectively. Typically, aerosol practitioners are interested in particle size. As such, the electrical mobility can be related to the particle mobility diameter,  $d_m$ , if the charge state of the aerosol is known.

A subset of DMAs used to size extremely small particles are known as High-Resolution Differential Mobility Analysers (HRDMA). Particle diffusion is one of the problems en-

countered when measuring particles smaller than 10 nm in size. Smaller particles diffuse more readily than larger ones, leading to increased particle loss and broadening the subset of particles selected by a classifier. HRDMAs remedy this by operating with extremely high sheath flow rates ( $> 100 \text{ L min}^{-1}$ ) and short working sections in order to reduce the residence of particles thereby minimising the effects of diffusion [47].

Particle mass analysers such as the Aerosol Particle Mass Analyser (APM) [45] or CPMA [145, 146] classify particles by their mass-to-charge ratio. Shown in Figure 1.2b, these classifiers balance an electrostatic force with a centrifugal force ( $F_C$ ) by passing an aerosol through an annulus between two concentric spinning cylinders with an electric field between them. The electrostatic force is proportional to the charge on the aerosol, whereas the centrifugal force is proportional to its mass. Therefore, only particles of the correct mass-to-charge ratio may exit the classifier. The CPMA provides an improved transmission efficiency compared to the Aerosol Particle Mass Analyser (APM) [145, 182] by rotating the inner cylinder faster than the outer cylinder, which creates a variation in force that acts to bring particles of the correct mass-to-charge ratio towards the centre of the classifier. The average mass-to-charge ratio selected by the CPMA is given by

$$s^* = \frac{m}{q} = \frac{eV}{\omega_c^2 r_c^2 \ln(\frac{r_2}{r_1})} \quad (1.02)$$

where  $V$  is the voltage difference between the cylinders,  $\omega_c$  is the rotational speed at the centre of the classifier,  $r_c$  is the central radius of the classifier, and  $r_1$  and  $r_2$  are the inner and outer radii respectively.  $q$  is the number of elementary charges on the particle, and  $e$  is the elementary charge on an electron.

The final classifier is the AAC (Figure 1.2c), which classifies particles by their mass-to-drag force ratio, referred to as particle relaxation time,  $\tau$ . The sampled aerosol is passed in the annulus between two rotating cylinders. Particles experience a centrifugal force, which is proportional to their mass and counteracted by a drag force. Only particles within a narrow band of relaxation times can exit the classifier. The average transmitted relaxation time for an AAC operating with balanced flow is given by

$$\tau^* = \frac{2Q_{\text{sh}}}{\pi\omega^2(r_1 + r_2)^2L}. \quad (1.03)$$

It should be noted that, unlike the DMA and CPMA, the AAC is a charge-independent classifier and does not require pre-charging of the aerosol before classification.

The aforementioned measurements of electrical mobility, mass and relaxation time can be related to equivalent particle diameters such as the mobility equivalent diameter ( $d_m$ ),

aerodynamic diameter ( $d_a$ ) and volume equivalent diameter ( $d_{ve}$ ) through the following relations [70]

$$\tau = m \frac{Z_p}{qe} = mB = \frac{C_c(d_a)\rho_0 d_a^2}{18\mu} = \frac{C_c(d_m)\rho_{\text{eff}} d_m^2}{18\mu} = \frac{C_c(d_{ve})\rho_p d_{ve}^2}{18\chi\mu} \quad (1.04)$$

where  $\mu$  is the gas viscosity,  $\rho_p$  is the material density,  $\rho_{\text{eff}}$  is the particle effective density,  $\rho_0$  is unit density and  $\chi$  is the dynamic shape factor and  $C_c$  is the Cunningham slip correction factor [70].

### 1.2.3 Transfer Functions

The transfer function of an aerosol classification system quantifies the probability of a particle of a given property passing through the instrument as a function of the system's operating conditions. The transfer function is required to operate aerosol classification instrumentation accurately and derive meaningful, accurate data from its raw measurements. An example of the transfer functions of aerosol classifiers depicted in Figure 1.2 are shown in Figure 1.3. Classifiers are inherently imperfect in that they do not precisely transmit particles of a single size, instead collecting a range of particles with similar properties illustrated by Figures 1.3a, b and c for the DMA, CPMA and AAC respectively. Both the DMA and CPMA are electrostatic-based classifiers and, therefore, require the aerosol to be charged in some way before classification. Figure 1.3d shows the product of the transfer function of the DMA with the charge distribution attained in a bipolar charger [218] illustrating multiple charge peaks in which larger particles carrying multiple charges behave in the same manner (*i.e.* same electrical mobility) within the DMA as the target size singly charged particle. This is similar to pairing a unipolar charger [49] with a CPMA, where multiple charge peaks can be seen (1.3e), which broadens the mass distribution exiting the CPMA. Accurate knowledge of charge distributions is necessary to predict the responses of these systems. The AAC (Figure 1.3f) is unlike the other two classifiers as it does not require particles to be charged, resulting in a truly aerodynamically monodisperse aerosol.

### 1.2.4 Tandem Aerosol Classification

An aerosol cannot be fully characterised by classification using a single particle metric, such as mobility, mass, or relaxation time, as other properties like particle morphology are often also of interest. Understanding particle shape is extremely important as it influences many other particle properties, such as optical scattering or capacitance [176], which affect particle charging. Measurement of particle morphology can be addressed by tandem aerosol

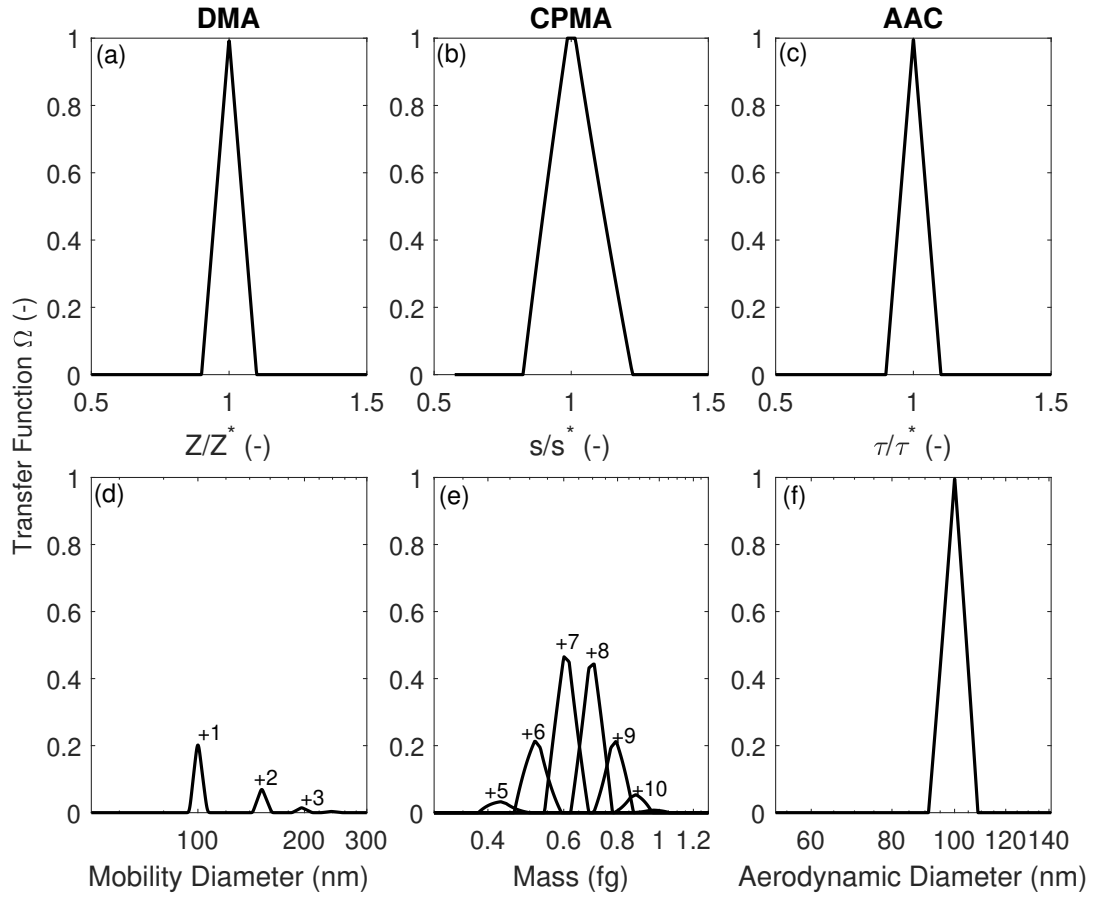


Fig. 1.3 Transfer functions of three commonly used aerosol classifiers. (a) a DMA diffusing transfer function in electrical mobility space [188], (b) a CPMA transfer in mass to charge space [182] (c) an AAC in non-dimensional relaxation time space [194]. The bottom rows of figures include transformations into appropriate classification domains, which include charge distribution formulations, specifically (d) includes Wiedensohler [218] bipolar charge formula and (e) uses Fuchs [49] charging theory to determine the unipolar charge distribution. The effects of diffusional broadening are minimal as the particles are 100 nm in size.

classification. Tandem classification refers to the experimental practise of placing two classifiers in series with one another, which allows for further characterisation of an aerosol through measurement of properties such as effective density [179, 154], hygroscopic growth [207] and even the aerosol charge distribution [80]. The pair-wise use of an AAC, CPMA or DMA can combine measurements of  $d_a$ ,  $m$  and  $d_m$ , respectively, to determine size-dependent effective density and shape factor of an aerosol through the use of Equation 1.04.

More recent work has seen the use of tandem classification as a means to determine the full two-dimensional mass-mobility distribution [161, 22, 178, 181]. Combining multiple classification techniques, such as particle mobility and mass, enables a comprehensive

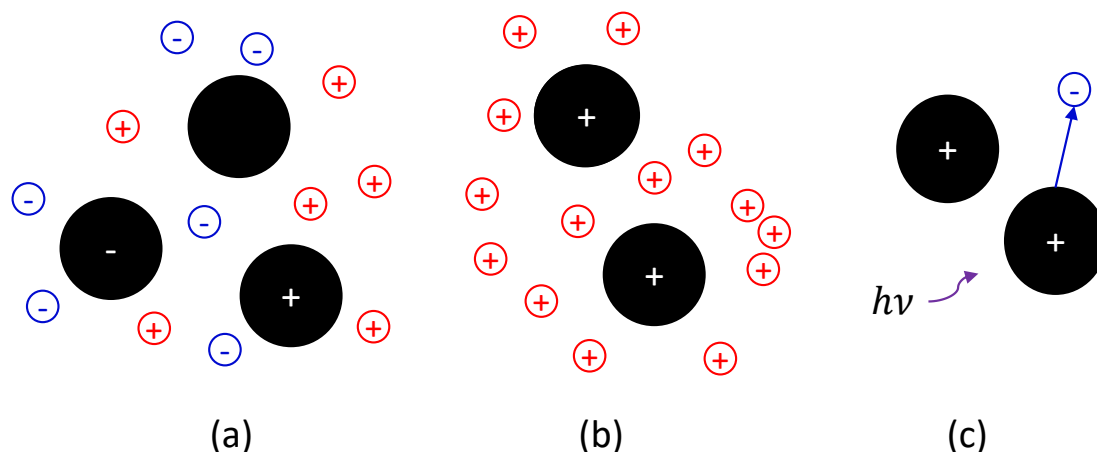


Fig. 1.4 Diagram of three commonly used aerosol charging techniques (a) Bipolar Diffusion Charging, (b) Unipolar Diffusion Charging, (c) Photoelectric Charging

characterisation of the entire aerosol population. It allows for the resolution of not only the particle size and mass but also the distribution of particle morphologies, providing deeper insight into the heterogeneity of aerosols [202, 183, 132]. This method enhances the ability to analyse complex aerosol mixtures, where particles may differ not just in size and mass but also in shape and structure, which can significantly influence their behaviour, transport, and impact on human health. By capturing the full range of particle properties, tandem classification paves the way for more accurate modelling of aerosol dynamics and a better understanding of the relationship between aerosol properties and their effects.

### 1.2.5 Aerosol Charging

Charging techniques play a crucial role in aerosol science, as many aerosol measurement and classification methods, in both low-cost sensors (LCS) and high-precision instrumentation, require particles to be charged before measurement. Three common charging mechanisms—bipolar diffusion charging, unipolar diffusion charging, and photoelectric charging—are illustrated in Figures 1.4a, b, and c, respectively. Among these, diffusion charging is the most widely used, wherein particles acquire discrete charge states through the attachment of ions via diffusion. Diffusion charging can be further categorized into two types: bipolar diffusion charging (Figure 1.4a), sometimes referred to as neutralisation, and unipolar diffusion charging (Figure 1.4b).

In bipolar charging, an aerosol is exposed to a balanced mixture of positive and negative ions, resulting in a steady-state charge distribution on the particles. Ionisation of the gas

molecules is typically achieved through radioactive decay [35, 111], X-ray ionisation [72, 197], or dual corona ionisation [169, 2], although other methods have also been demonstrated [158, 193, 65]. The ions transfer charge to the aerosol particles through ion-particle collisions, leading to a distribution of positively, negatively, and neutrally charged particles [218, 49, 71]. When sufficient ions are present, and the aerosol remains in the ionisation region for an adequate time period, a well-defined charge distribution is achieved, where the fraction of particles with a specific charge remains constant over time [41, 73]. This stability in the attained charge distribution is a key advantage of bipolar charging.

In contrast, unipolar charging transfers charge to particles using ions of a single polarity, typically generated via corona discharge, though other methods can be employed [74]. Unipolar charging is more efficient than bipolar charging in terms of intrinsic charging capacity but does not produce a clearly defined charge distribution. The charging efficiency in this method is determined by the  $n_i t$  product, where  $n_i$  is the ion number concentration, and  $t$  is the residence time in the ion region [19]. However, unipolar charging enables particles to attain significantly higher charge levels, which is advantageous in applications where measuring charged particle currents is essential, as it improves the signal-to-noise ratio.

Both diffusion charging methods—unipolar and bipolar—are critically influenced by the properties of the ions used, particularly their mass and mobility. Understanding these ion characteristics is key to solving the equations governing aerosol charging dynamics on spherical particles [49, 71, 163]. Environmental factors such as humidity [114], ion ageing time [7], carrier gas composition [186], and gas-phase contaminants [187] can significantly impact these ion properties, thereby affecting the efficiency and predictability of the charging process.

One effective way to study these small ions is through high-resolution differential mobility analysis, which provides precise measurements of ion size. These measurements can offer valuable insights into ion behaviour and their response to various environmental conditions [47], making it particularly useful for investigating the influence of carrier gas composition on ion size and concentration.

Photoelectric charging is the third most commonly used charging technique. However, it is less frequently employed than the diffusion charging methods due to its high sensitivity to the material properties of the particles [136]. In contrast to diffusion charging, which relies on ion-particle collisions, photoelectric charging directly ionises particles through exposure to ultraviolet (UV) light (Figure 1.4c). When particles absorb photons with sufficient energy, they emit electrons, which then collide with gaseous molecules to form negative ions [117, 138]. This direct ionisation process can result in higher charging efficiency than diffusion charging, which relies on the collisional transfer of charge. However, the effectiveness of

photoelectric charging is heavily influenced by the material properties of the aerosol particles, as well as the intensity and wavelength of the UV light used [177, 91, 97, 24, 170, 136].

### 1.3 Problem Statement and Scope

Engineered aerosol particles are essential in various industrial applications, such as the production of battery materials, powders, spray-dried products, and drug formulations. Fine control over aerosol properties is crucial for optimising performance and ensuring product quality in these fields. Beyond industrial use, aerosol science is critical in understanding environmental and health-related impacts, as aerosols can significantly affect air quality and human health. Over the years, substantial advancements have been made in aerosol characterisation techniques, allowing for more precise measurements of aerosol properties such as size, concentration, and morphology. However, key challenges persist in fully understanding the behaviour of aerosols under varying environmental conditions.

Specifically, the influence of RH on aerosol charging dynamics remains inadequately explored. Although RH is known to affect ion properties, its impact on charging efficiency and charge distribution is not well understood, particularly for portable charging sensors. Comprehensive studies are needed to investigate the effects of RH on aerosol charging processes across different charging mechanisms, such as bipolar and unipolar diffusion charging, and how these changes influence the accuracy of aerosol measurements.

Additionally, despite advances in aerosol sizing techniques, the accurate determination of the mass distribution of polydisperse aerosols remains a significant challenge, particularly with particle mass analysers. While tools such as the CPMA and APM have been used in tandem applications to measure particle morphology and obtain mass distributions, they are rarely employed as single classifiers due to issues with neutral particle penetration when used with a bipolar charger [191, 180]. This work explores the use of the CPMA by pairing it with a unipolar charger. However, this approach introduces additional challenges, including multiply charged particles and uncertainties in the relationship between mass, mobility, and charge, which this work aims to address.

### 1.4 Organisation of Thesis

Following this chapter, Chapter 2 provides a review of the existing literature, organised into two main sections. The first section focuses on the theory and measurement of particle charging, with an emphasis on measurements that are particularly relevant to changes in relative humidity. The second section covers measurements of particle size distributions and

tandem aerosol classification, with particular emphasis on mass distribution measurements and the determination of effective density. The research gaps identified in this review form the basis for the objectives outlined at the end of the chapter.

Chapter 3 investigates the effect of relative humidity on three different particle charging methods by measuring the mean charge as a function of particle size and ion-mobility spectra using an HRDMA.

Chapters 4, 5, 6, and 7 all explore the use of unipolar diffusion chargers in conjunction with existing classification techniques. Chapter 4 experimentally investigates multiple charge correction methods in particle mass analysers. Chapter 5 details the validation of a new particle classifier, the Mobility Separator Electrometer (MSE), through numerical modelling and experimentation. Chapter 6 highlights the potential pitfalls of determining size-resolved particle mass distributions using a CPMA. To address these issues, Chapter 6 also introduces a new system, the Mass Mobility Aerosol Spectrometer ( $M^2AS$ ), which demonstrates methods to determine mass distributions from a unipolar-CPMA system. These methods are greatly aided by the additional measurements provided by the MSE. The chapter delves into the technical details and methodologies employed in the  $M^2AS$ , highlighting its capabilities and advantages in analysing aerosol mass distributions. Chapter 7 provides experimental validation of the  $M^2AS$  system, including measurements of particle effective density, particle distributions, and integrated concentration. Finally, Chapter 8 summarises the main conclusions of this work and suggests directions for future research.



# Chapter 2

## Literature Review

The first part of this chapter describes theoretical and experimental advances in aerosol particle charging. Particular focus is given to work performed to investigate the effect of humidity on particle charging. Finally, measurements of ions directly produced by charging sources, which are typically sub 2 nm, are discussed. The second part discusses particle size distribution measurements, focusing on mass and mobility distributions as well as the determination of classifier transfer functions. The final part discusses tandem classification, a powerful technique for evaluating particle morphology.

### 2.1 Particle Charging

#### 2.1.1 Diffusion Charging

Diffusion charging is the process of particles gaining charge through the attachment of ions undergoing Brownian motion. The attachment kinetics are governed by the particle size as well as several ion properties, including the ion mass, mobility and speed distributions. The most commonly used charge theory for spherical particles was developed by Fuchs [49]. Fuchs' theory is known as the limiting sphere theory, in which an imaginary spherical surface concentric to the particle's surface is assumed. For radii greater than the limiting sphere, ions are assumed to behave according to the continuum transport equation, whereas, within the limiting sphere, ions particles are modelled as moving in a vacuum following the kinetic theory of gases. Matching the flux at the limiting sphere surface according to the two mechanisms with further considerations yields a combination rate coefficient,  $\beta$ , which is defined to quantify the rate of collision between ions and particles. The combination coefficient is used within population balance equations to solve the particle charge distribution. To fully describe the charging process, accurate knowledge of the ionic properties, such

as mobility, mass, concentration, residence time within the charging zone, and underlying pressure and temperature conditions, is needed. A more detailed description of the calculation of the combination coefficient is provided in Appendix A.

Within aerosol science, methods are required to obtain repeatable charge distributions, enabling particle size distribution measurements. This is typically done using either bipolar or unipolar diffusion charging, which are discussed below.

### Bipolar Charging

When an equal mixture of positive and negative ions is present, the aerosol is said to undergo bipolar diffusion charging. Given sufficient ion-to-aerosol concentration, in a bipolar charging environment, the charge state of an aerosol will reach a steady state condition in which the rate at which particles with  $q$  charges charge to  $q + 1$  due to positive charge transfer is equal to the rate at which particles with  $q + 1$  discharge to a  $q$  state due to negative charge transfer [163, 197]. Bipolar charging underpins one of the most commonly used particle analysis techniques, differential mobility analysis. A common approximation to the steady state charge distribution given by Wiedensohler [218] enables rapid calculation to enable fast particle size analysis. The attainment of a steady-state charge distribution is assumed in many applications. However, there have been many studies demonstrating that the charge distribution can deviate from theory in several scenarios including: low residence times through the charger [80, 78, 223], charging of smaller particle sizes ( $< 20$  nm) [73, 41], charging of non-spherical particles [81, 57], type (*e.g.* radioactive compared to Soft X-ray) and strength of the ionisation source used [80, 78] and water vapour content [72, 102]. Furthermore, the types of ions produced can vary depending on system contaminants [187], water vapour content [114, 102], and the type of ionisation source [87]. In a numerical study by Tigges et al. [197], a sensitivity analysis was conducted concerning bipolar chargers to evaluate sensitivity to ion mobility values. Based on measured variability in literature values of ion mobilities, the deviation in charge fractions could be as high as 40%. Notably, they observed that for particles larger than 40 nanometers, the ratio of ion mobilities played a crucial role rather than the absolute magnitude of either mobility. This underscores the importance of accurate knowledge of the ion properties within the charger.

Bipolar charging can also be used in low-cost sensing applications [141]. Gunn proposed a simple model demonstrating that the steady-state charge on an aerosol in a bipolar environment depends on the ratio of ionic conductivity,  $n_+Z_+/n_-Z_-$ . Assuming that the number of positive and negative ions is approximately equal ( $n_+ = n_-$ ), this expression simplifies to the ratio of ionic mobilities. Using these assumptions, Nishida et al. [141] found a linear

relationship between particle mean charge and diameter for monodisperse, spherical particles with diameters ranging from 50 nm to 1000 nm.

### Unipolar Charging

Unipolar charging produces a high flux of a single polarity of ions, either positive or negative, which diffuses towards the particle. The ion concentration-time product,  $n_i t$  is the most critical parameter in characterising unipolar diffusion chargers. Unlike bipolar charging, in which given a sufficient  $n_i t$ , the particle charge distribution becomes invariant with time, the charge level per particle continually increases with the  $n_i t$  product in a unipolar ion environment. The benefit of a unipolar charger arises when paired with electrometer-based measurements. Here, integrated current signals are measured by depositing particles on an electrically isolated filter. The use of a unipolar charger significantly increases the signal-to-noise ratio. The simplest way to generate unipolar ions is a corona discharge, which is produced by a non-uniform electrostatic field commonly applied between a grounded surface and a thin wire or needle. The electric field accelerates ions already present within the charging volume (*e.g.* existing through cosmic radiation). An electron will collide with a neutral gas molecule, producing another free electron. This process continues, producing an electron avalanche and a dense plume of positive ions and free electrons. A positive corona occurs when a positive voltage is applied to the needle/wire electrode. The electric field is directed away from the needle towards the ground electrode. Therefore, the electrons are pulled towards the needle/wire, and the positive ions are driven towards the ground electrode. Multiple designs of unipolar chargers used in aerosol applications aim to increase particle charge and minimise particle losses. Designs and performance characterisation for a range of chargers have been summarised by Intra and Tippayawong [74].

Note that while this section focuses on diffusion charging of aerosols, field charging in unipolar chargers can also play an important role. Here, ions follow electric field lines imposed by an external electric field, which converge on the particle, transferring charge. This mechanism is separate from diffusion charging. The two phenomena can be superimposed to determine the combined effect of field and diffusion charging. Field charging scales with the square of the particle diameter and, therefore, is the dominant charging mechanism for particles larger than 1  $\mu\text{m}$  [70, 217].

#### 2.1.2 Photoelectric Charging

Depending on their optical properties, aerosol particles can absorb a high-energy photon, resulting in the emission of a photoelectron. This process is known as the photoelectric effect

and can be used to charge aerosol particles by exposing them to UV light or soft X-rays. Initial work by Schmidt-Ott and Siegmann [171] demonstrated the applicability of photoemission for measuring the photo-emissive properties of molybdenum oxide particles suspended in dry air. By using an oscillating electric field, they measured particle concentration and photoelectric yield and compared them to a simplified model of charging and recombination. The Fowler-Nordheim law, suitable for the photoemission of electrons from flat surfaces, was extended to apply to aerosol particles [170].

According to the model of Burtscher et al. [26] the charging process by photoemission can be described by four sequential steps. The first step is the absorption of a photon and excitation of an electron from the particle. The absorption of light depends on both the optical and geometrical properties of the aerosol particle. After absorption, the excited electron moves to the particle surface and overcomes the surface potential, leading to its emission. In order to emit a photoelectron, the energy of the photon has to be higher than the work function of a particle holding charge  $q$ . This relationship is described by the Fowler-Nordheim equation:

$$Y = K_c(h\nu - \Phi^{q \rightarrow q+1})^m \quad (2.01)$$

where  $Y$  is the electron yield per incident photon,  $h\nu$  is the photo energy,  $\phi$  is the work function of the material and  $K_c$ , depends upon light intensity, absorption, geometry and duration of radiation.  $m$  is an empirically determined constant, which is approximately 2 for metals and soot particles [139]. The probability of photoelectric charging occurring is given by the combination coefficient  $\alpha^{q \rightarrow q+1}$ ,

$$\alpha^{q \rightarrow q+1} = Y \frac{I}{h\nu} \sigma_{ph} \quad (2.02)$$

where  $I$  is the irradiation intensity and  $\sigma_{ph}$  is the photoelectrically active surface area. For a perfect sphere  $\sigma_{ph} = \pi d^2$ , for non-spherical particles with surface adsorbates,  $\sigma_{ph}$  is dependent on the state of the surface and morphology of the particle. Once the photoelectron is emitted, it will undergo diffusion, colliding with gas molecules and creating gaseous ions. Recombination can occur as the now positively charged particle attracts the highly mobile negatively charged gaseous ion. In order to prevent recombination an external electric field can be applied.

Once an electron is emitted, the work function increases according to

$$\Phi^{q \rightarrow q+1} = \Phi_\infty + \frac{e^2}{2\pi\epsilon_0 d} \left( q + 1 - \frac{5}{8} \right) \quad (2.03)$$

where  $e$  is elementary electron charge, and  $\epsilon_0$  is the vacuum permittivity. The  $q + 1$  term represents the Coulomb force between a released electron and the remaining charged particle; after each electron is released, the Coulomb force increases and opposes further release. The negative  $5/8$  term denotes the image force.

Photoemission yield has been demonstrated to be proportional to total mobility surface area ( $d_m^2$ ) in the free molecular and transition regimes ( $10 < d < 100$  nm) for a range of metals such as silver and gold [136, 25, 91], stripped diesel particles [97, 136] and graphite particles coated in PAH [134]. Based on these studies, in situ measurements of particle surface area are possible. However, the measure of mobility surface is a strong function of both particle material and morphology. In this regard, it is hard to isolate the response of a single material within a heterogeneous aerosol sample.

### 2.1.3 The Effect of Relative Humidity on Particle Charging

The aforementioned diffusion and photoelectric charging techniques are frequently used in low-cost portable devices. These devices provide a low-cost method of measuring particulates, and studies have shown that low-cost charging sensors can measure metrics relevant to environmental and personal exposure monitoring to within  $\sim 30\%$  of laboratory grade instrumentation [66, 100, 77]. Deployable aerosol charging sensors are, therefore, used in a wide range of environments. However, one parameter which has not been studied extensively for such measurement techniques is the response to changes in humidity. In ambient environments, relative humidity (RH) can vary spatially and temporally depending on geographic location.

Unipolar charging is the most commonly used charging mechanism in ambient low-cost measurements due to the high intrinsic charge efficiencies, which result in highly charged particles and a good signal-to-noise ratio. The integrated current has been shown experimentally to be linearly dependent on number concentration and scales with a power law with respect to particle size where the exponent varies from 1 - 1.3 [199, 125, 48, 85, 13, 99]. Unipolar charging of particles does not achieve a steady-state charge distribution, and the charging conditions need to be controlled in order to obtain a repeatable charge distribution.

Previous studies investigating the effect of RH have focused on numerically and experimentally determined voltage-current discharge characteristics [222, 143, 214]. Xu et al. [222] proposed a modified formula for the voltage required to initiate a corona discharge. This modification takes into account the enhanced conductivity of air at higher humidity, which results in a reduction of the voltage required for a sustained corona discharge. Yawootti et al. [225] found the effect of RH on the discharge current from their needle charger was a strong function of the polarity as well as the magnitude of the applied voltage. For positive

voltages less than  $\leq 2.7$  kV, the discharge current increased by up to 2 orders of magnitude as RH increased from 20 - 90%. For higher applied voltages ( $> 2.7$  kV), the effect of RH was found to be less drastic, observing approximately invariant discharge currents across the humidity range. On the other hand, for negative applied voltages  $\leq 2.7$  kV, the discharge current increased by approximately four orders of magnitude. Young et al. [228] studied the effect of RH on the charging of dry powder inhalers. However, the RH pertained to the value of the powder storage humidity rather than the working humidity of the Electrical Low-Pressure Impactor (ELPI) used to characterise the charge distribution in the study, which was maintained at 45%. Ambient measurements taken with an electrostatic PM<sub>10</sub> sampler by Yawootti et al. [226] exhibited slightly different linear relations with a tapered element oscillating microbalance when the RH was above and below 60%. However, within this work, it is stated that the incoming aerosol stream sampled by the electrostatic sampler was first passed through a diffusion dryer and as such, the charger conditions should not have been affected by the ambient humidity. In addition, the overall variability in the linear relation was less than 8%. Jung and Kittelson [85] found that the stability of diffusion charger was correlated to relative humidity. Fluctuations in response were reduced by renewal of the silica dryer upstream of the chargers.

As the ion concentration and mobility dictate the charging performance of unipolar chargers, some studies have looked at how humidity affects ion formation. It is commonly assumed the hydrated proton  $H^+(H_2O)_n$  with a mobility of  $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and mass of 109 amu is the most abundant ion within a charger at 10% humidity [157]. However, it is well known that ion properties are dependent on the gas composition [99, 187]. Mohnen [129] proposed a set of chemical reactions that lead to the formation of a stable, heavier hydrated proton with three attached water molecules. Kebarle et al. [90] demonstrated the relative concentration of hydrated proton ions is a function of the partial pressure of water vapour and temperature. Manninen et al. [121] characterised the ion mobility distribution produced by a corona needle used within a mass spectrometer. The corona ion size distribution, in terms of the number of peaks and the concentration of both positive and negative ions, changed as a function of RH, suggesting the presence of different ion species. In general, they found that as humidity increased, the size of the ions increased. They also found that placing a silica dryer into an already dried ( $RH \sim 0.6\%$ ) compressed air stream resulted in a significantly different distribution of ions, indicating that contaminants play a role in the ion distribution.

Bipolar charging or 'neutralisation' is the most commonly used technique when paired with particle mobility analysers, wherein particles are subject to a bipolar ion environment for a sufficient time such that a steady-state charge distribution is reached [71, 49]. Charging performance is affected by many parameters, but investigations into the effect of humidity

are comparatively small. Some authors have investigated how RH influences ion composition and mobility. Hye et al. [72] and Liu et al. [114] both evaluated the performance of a soft X-ray neutraliser as an alternative to radioactive sources. In doing so, they measured the mobility distribution of ions produced in dry and humid nitrogen. Hye et al. found the peak of the negative ion distribution shifted significantly with the addition of water vapour to higher electrical mobilities for negative ions (i.e. became smaller in size <sup>1</sup>) whilst the peak of the positive ion only became slightly more mobile. A more recent study on a commercially available soft X-ray source (Model 3087, TSI, Inc., USA) by Liu et al. [114] found contradicting results, showing that the dominant negative ion decreased in mobility as humidity increased, whereas positive ion mobility remained approximately invariant. In addition, they paired their mobility measurements with a mass spectrometer, which garners further information on the chemical composition of ions of a given electrical mobility. Their observations suggested that negative acid radical ions cluster with water molecules, whereas the concentration of the hydrated proton dominates the positive mobility spectrum in higher humidity. However, significant fragmentation within the mass spectrometer made it difficult to truly elucidate the chemical constituents of the ions. Recent atmospheric studies using an SMPS have highlighted that changes in RH can cause deviations in size distribution metrics [109]. At higher RH (> 60%), the integrated number concentration of particles measured by two SMPS, one operating with a <sup>85</sup>Kr and the other with a Soft X-ray charger, was overestimated by up to 60% when compared to a reference CPC.

Photoelectric chargers are the least commonly used chargers owing to their sensitivity to particle material and dependence on the state of the particle surface. Condensed/adsorbed species such as Polycyclic aromatic hydrocarbons (PAHs) can be bound to the particle surface and act like an antenna, drastically increasing the photoelectric response of the particle [149, 24]. To our knowledge, there have been no studies on the effect of RH on photoelectric charging. However, studies have shown that water molecules not only absorb UV light [148] but can undergo a series of chemical reactions that produce water droplets [227].

### 2.1.4 Effect of Particle Morphology on Diffusion Charging

It is well known that both unipolar and bipolar charging are affected by particle morphology. Particle charging theories like those of Fuchs [49] strictly apply to spherical particles. The dynamics of ions in the presence of non-spherical particles becomes significantly more complicated. Chang [30] developed a theory to determine the charge of arbitrarily shaped

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<sup>1</sup>Size refers to equivalent electrical mobility diameter

aerosols. The main emphasis of their work was to demonstrate that in the continuum regime, the mean charge is determined by electrical capacitance. In contrast, in the free molecular regime, it is determined by geometric surface area, with a weaker dependence on particle capacitance. More recent models have utilised Brownian dynamics simulations to calculate the charge acquired on non-spherical particles [56, 108, 58].

A large number of experimental studies have demonstrated the differences between the charging of spherical and non-spherical particles of the same mobility size. Jung and Kittelson [85] found that soot particles from a diesel engine acquired approximately  $\sim 15\%$  more charge than sodium chloride particles for mobility equivalent sizes between 30 nm and 150 nm. Shin et al. [176] found that the mean charge of both spherical and agglomerate silver particles was proportional to the mobility diameter between 30 nm and 200 nm, and on average agglomerates attain 24% more charge for the same mobility diameter. Oh et al. [144] demonstrated that fractal  $\text{TiO}_2$  particles can charge by up to 30% more than spherical particles; however, the extent to which a particle attains more charge is dependent on the particle fractal dimension. Particles with a lower fractal dimension, and therefore larger surface area and self-capacitance for the same mobility diameter, attain more charge. Even more striking is the difference in charging between spheres and rod-like particles. Park et al. [153] compared the charging performance of silver nanowires and Polystyrene latex spheres (PSL) with mobility diameters between 200 nm and 300 nm. They found that silver nano-wires had between 66% - 109% more charge than their spherical counterparts. This was attributed to the increased capacitance of the nano-wires relative to the spherical PSL.

Bipolar charging has also been shown to be influenced by particle morphology. Rogak and Flagan [165] measure the uncharged fraction of spherical and non-spherical particles, finding that the uncharged fraction of titanium oxide agglomerates was smaller than spherical particles for the same mobility diameter. Multiple authors have also shown that the charging of soot particles is preferentially negative and results in a broader charge distribution [123, 221, 81]. To account for differences in charging between spheres and non-spherical particles, the concept of an equivalent charging diameter is often used, which enables correction of the particle charge distribution [165, 81].

The discrepancy between the charging of spherical and non-spherical particles can lead to errors in data inversion in instruments that utilise diffusion chargers. Due to the increased charge acquired by aggregates relative to spherical particles, they can be miss-sized in electrical mobility-based measurement techniques. This has been demonstrated for a range of fast particle spectrometers, all of which use unipolar chargers [230, 10, 213, 150]. Deviation of bipolar charge distributions when classifying non-spherical particles can also potentially alter SMPS measurements [81, 123]. Therefore, the effect of morphology on charging must

be considered either through calibration or direct measurements of charge to obtain accurate data when using diffusion chargers in systems that infer particle size from measurements of particle electrical mobility.

### 2.1.5 Measurement of Charging Ions

As the ion properties are extremely important in particle charging, it is crucial to develop techniques which enable the characterisation of small particles. The ions produced by particle chargers consist of a range of chemical species with equivalent mobility diameters ranging from 0.9 nm to 2 nm. Mobility measurements within this size range are extremely difficult with conventional DMAs owing to significant diffusive loss and broadening of the classifier transfer function [190]. In initial studies of ions, authors used TSI nano DMAs operating with non-diffusing resolutions of 20 [102, 103]. However, as later work has shown, this can lead to erroneous observations due to significant broadening of the transfer function [215]. To tackle the problem of sub 2 nm sizing, it is required to greatly reduce the residence time within the classifier by using extremely large flow rates. This has led to the development of HRDMAs which operate with flow rates in excess of  $100 \text{ L min}^{-1}$  [40, 206]. By increasing the sheath flow rate and reducing the volume of the working section, the residence time is greatly reduced, allowing for improved transmission and classifier resolution, which in turn enable significant improvements in the accuracy of ion measurements [185, 40]. They can also be coupled with mass spectrometers to measure the full mass-mobility distribution of ions produced within an aerosol charger.

Alonso et al. [7] claimed to provide the first measurements of charger ions using differential mobility analysis. They concluded that the mobility distribution of air ions strongly depends on their residence time before measurement and, in the case of ions generated by corona, on the extent of electrostatic losses within the ionizer. Steiner and Reischl [187] investigated the dependency of the ion mobility distributions on carrier gas contaminants caused by the evaporation of trace gases from commonly used sample tubing. It was found that impurities in the carrier gas can dramatically change the mobility of ions present within a system. Kallinger et al. [87] measured the ion distribution of four different aerosol chargers and found that the positive ion spectra were similar for all chargers however, the negative ion spectra differed depending on the charging mechanism. Steiner et al. [186] paired an HRDMA with a mass spectrometer to identify the chemical constituents of negative ions. They determined the nitrate ion,  $\text{NO}_3^-$ , was the dominant negative ion. Maißer et al. [118] performed similar experiments, measuring the mobilities and mass-to-charge ratios of 6 positive ions and 25 negative ions produced by a  $^{210}\text{Po}$  source in dry air, and concluded that the positive ions were generated by protonation, while the negative ions were all deprotonated.

More recent work has identified the effect of water vapour concentration on the mass and mobility of the ions produced within a Soft X-ray charger [114].

It should be noted that in all the aforementioned ion studies, only the work of Steiner and Reischl [187] has explicitly tried to account for the transfer function of the experimental system. Within their work, they found that the total concentration of negative ions produced by an  $^{241}\text{Am}$  charger, taken by integrating the measured number distribution, differed by an order of magnitude between different measurement conditions. It would be expected that the steady concentration of ions would be produced regardless of the condition of the carrier gas. They corrected their measurements by taking into account an effective length which predicted a particle penetration through the system of 0.5% for 1 nm ions compared to an 8% penetration of 1.5 nm. Other work utilising HRDMAs has performed inversion using the non-diffusing triangular transfer function of the DMA, which is a questionable practice at these size ranges where diffusion is a dominant loss mechanism [159, 215].

Owing to significant ion loss, as well as the indicated order of magnitude difference in penetration between 1 nm and 1.5 nm ions, correct inversion of raw concentration measurements is extremely important, as this can impact reported measurements of average ion mobility (which are often used in charge distribution calculations) and total ion concentration. For approximately mono-modal ion spectra, the effect of inversion on the average ion mobility will be negligible (*e.g.* see Figure 6a in [186]). However, the same cannot be said for distributions like those in Figure 5a in [186] in which a broad distribution with multiple peaks is observed. There is, therefore, a need to correct raw ion mobility measurements in a manner which takes into account the full transfer function of the system in an accurate manner.

## 2.2 Particle Size Distribution Measurements

### 2.2.1 Mobility Measurements

Differential mobility analysis is the most widely used method for determining particle size distributions. It is typically carried out by combining a bipolar charger, DMA, and CPC. Originally introduced by Knutson and Whitby [98], differential mobility analysis has been a key technique in aerosol science for over four decades. The DMA operates by selecting particles based on their electrical mobility, which is distinct from the mobility diameter of the particles. To convert electrical mobility to particle size, the particle charge state must be accounted for. If particles were to acquire only a single charge, this would be straightforward, but bipolar charging results in a range of charge states depending on factors such as particle

size, morphology, composition, and even the type of charger used [56, 218, 81, 197, 196]. As a result, a correction for multiple charges is necessary, as larger particles with multiple charges can exhibit the same electrical mobility as smaller particles with a single charge [67]. A significant limitation of SMPS measurements is the uncertainty in the particle charge distribution, which can be of the order of 20 - 30% [81, 196, 106]. Inaccuracies in the representation of this charge distribution can lead to biases in the inferred particle mobility size distribution [106].

For mobility distribution measurements, the DMA column voltage is typically varied exponentially with time [211], and the concentration downstream of the DMA is measured. This configuration is known as a Scanning Mobility Particle Sizer. SMPS scans usually take 2-3 minutes; any faster, and the transfer function of the DMA becomes significantly distorted [34].

Other mobility sizing techniques aim for faster measurement acquisition, typically operating at a frequency of 1 Hz or less. These instruments, referred to as fast particle sizers, generally consist of a unipolar charger and electrostatic classifier column, incorporating rings of electrometers to measure the current produced by the charged particles as they are collected [18, 150, 230, 10]. While they offer better time resolution compared to the SMPS, they generally have poorer sizing resolution and require sufficiently high particle concentrations to obtain accurate current measurements.

### 2.2.2 Mass Distribution Measurements

Mass is a particularly useful metric to quantify an aerosol as, unlike equivalent particle diameters, it is intrinsic to the particle. It is, therefore, not affected by particle structure or the prevailing conditions of the carrier gas such as pressure and temperature<sup>2</sup>. In spite of this, particle mass analysers such as the CPMA or APM are not typically used to measure number-weighted or mass-weighted mass distributions. The primary reason for this pertains to issues with data inversion. When PMAs are paired with bipolar chargers a significant fraction of smaller particles are neutral. Smaller neutral particles can penetrate PMAs at lower rotational speeds as they experience no electrostatic force and the centrifugal force is insufficient to remove them from the flow. This effect is demonstrated in Figure 2.1a, which shows the transmitted particle mass as a function of the CPMA set-point when combining a bipolar charger and a CPMA. The transmission of smaller particles is significant in the lower right-hand portion of the figure when selecting particles of a larger mass. The particles within this region are all neutrally charged. All of these particles would be counted equally

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<sup>2</sup>Note that the transfer function width of mass analysers is still affected by particle structure, pressure and temperature owing to particles drifting across the classification gap [145, 182]

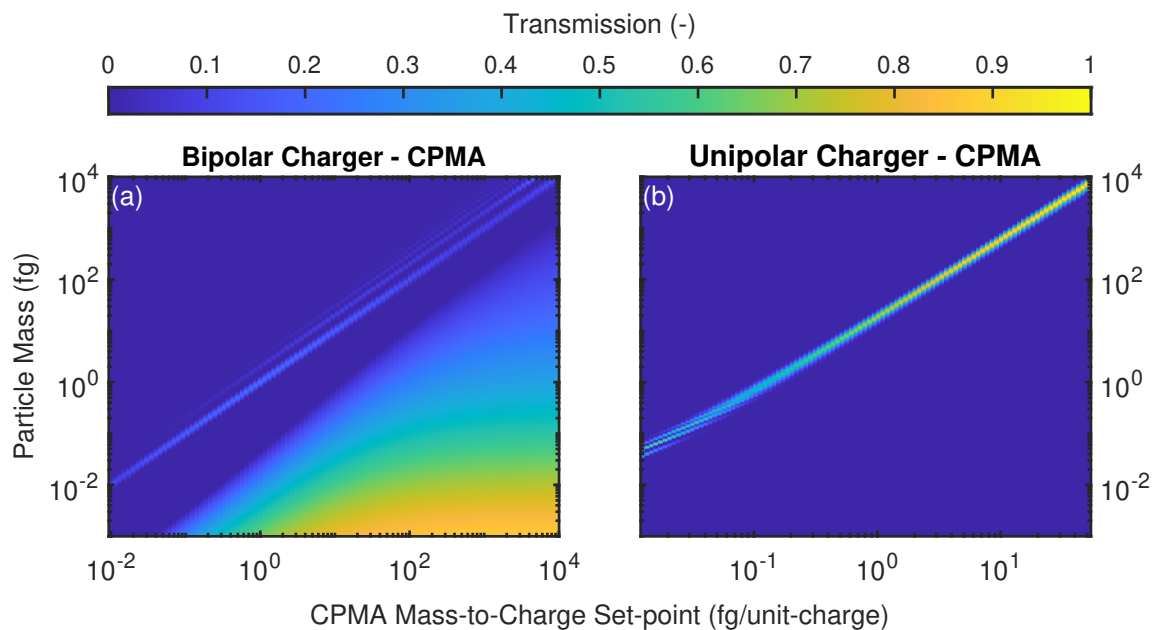


Fig. 2.1 Transmitted Particle Mass as a function of CPMA set-point by a combination of an aerosol charger and CPMA. (a) combination of a bipolar charger [218] and CPMA transfer function [182]. (b) combination of a unipolar charger ( $n_{it} = 5 \times 10^{13} \text{ s m}^{-3}$ ) [49] and CPMA transfer function [182]. Note that the CPMA mass-to-charge set-points (x-axis) in the unipolar case are smaller than the respective bipolar case owing to the fact the particles are multiply charged.

by a particle counter, making data inversion at larger sizes extremely difficult. The extent to which neutral particles influence bipolar-charger CPMA measurements depends on the size distribution of the aerosol being measured and the operating resolution of the CPMA.

Several authors have demonstrated that pairing a PMA with a unipolar charger can alleviate the influence of neutral particles; however, an additional problem of accounting for multiply charged particles is incurred [191, 180, 36]. This is illustrated in Figure 2.1b where the swathe of smaller particle penetration that is exhibited in the case of the bipolar-CPMA combination is not exhibited<sup>3</sup>. Symonds et al. [191] initially demonstrated that the combination of a unipolar charger-CPMA and an electrometer can be used to determine the particle mass concentration of an aerosol, enabling faster calibration of instrumentation that measures mass-concentration compared to conventional gravimetric methods. This methodology is called the CPMA—electrometer reference mass standard (CERMS). It has been shown to provide good repeatability [198] and has been utilised in a number of calibration and absorption characterisation studies [44, 37, 36, 174].

<sup>3</sup>The extent to which neutral particles impact unipolar charger-CPMA measurements is dependent on the ion-time product the charger is operated at

More recently, originating from initial work by Corbin et al. [36], Sipkens et al. [180] showed that the average mass transmitted through a unipolar charger PMA system can be estimated to within  $\sim 30\%$  for a range of experimental conditions using a series of average charge algorithms which allows for near real-time multiple charge correction. Although useful to approximate the average transmitted mass through a unipolar charger PMA system, this method cannot truly determine sampled mass distribution. Determination of the sampled mass distribution from count measurements downstream of a unipolar PMA system has not been done before as it requires accurate knowledge of the classifier transfer function, which in turn relies on knowledge of the relationship between mass, mobility diameter and charge for a given particle. While these measurements are possible, they require significant experimental time and equipment, which is not often feasible for use within a study.

Size-resolved mass distributions can be measured with other techniques e.g. cascade impactors such as the Microorifice Uniform Deposit Impactor (MOUDI). Such measurements typically involve gravimetric measurements of mass collected on impactor substrates. Whilst this provides a method of mass distribution measurement, it suffers from the same drawbacks of gravimetric analysis, namely the requirement of long sample times. Chen et al. [31] developed a quartz crystal microbalance (QCM) based instrument for real-time aerosol mass distribution measurement using a six-stage QCM micro-orifice cascade impactor. This allowed for real-time mass measurements the resonance frequencies of the QCMs decrease proportionally to the mass of the deposited aerosol. However, it suffers from low sizing resolution owing to the limited number of impactor stages.

Tandem or parallel classification can also be implemented to measure mass distributions - this and similar techniques are discussed in section 2.3.

### 2.2.3 Analytical Methods for Determining transfer functions

Paramount to obtaining size distributions is knowledge of the instrument transfer function. Knutson and Whitby [98] first calculated the analytical form of the non-diffusing DMA transfer function. This formulation involved defining a stream function for the flow within the DMA, which can be described as incompressible, rotational and axisymmetric with an analogous electric flux function. The particle moves in such a way that the ratio of the number of streamlines crossed to the number of electric field lines crossed is always equal to the particle's electric mobility,  $Z_p$ . A similar theory was also directly applied to the AAC by Tavakoli and Olfert [194] to determine its transfer function.

The theoretical CPMA transfer function was initially derived by Olfert and Collings [145], using a numerical finite difference scheme. This work showed that the CPMA has a trapezoidal shape due to the radial variation in force across the classifier gap. Reavell et al.

[162] proposed a simplified model of the CPMA, which assumes the force is constant over the gap of the CPMA, providing a triangular approximation of the CPMA transfer function. This simplified model is applied in commercial CPMA. More recent work by Sipkens et al. [182] utilised particle tracking methods to determine the CPMA transfer function, which compares extremely well to the work of Olfert and Collings [145] but with the added benefit of reduced computational costs. In addition, this work presented an expression for the transfer function that incorporates particle diffusion.

### 2.2.4 Monte Carlo Methods of Determining Transfer Functions

An extensive body of work has used Monte Carlo methods to determine and investigate particle classifiers. Monte Carlo methods typically involve solving the trajectory of particles with respect to time according to the radial and axial equations of motion of a particle within the classification region. Hagwood et al. [62] implemented this method for the determination of the transfer function of a new particle mass spectrometer, now known as the APM with the addition of diffusion into the calculation of the transfer function. Hagwood et al. [63] then employed this method to the DMA for comparison with the analytical non-diffusing DMA transfer developed by Knutson and Whitby [98]. They found that the effect of particle diffusion on transmission through the DMA was easily evaluated using Monte Carlo methods. Other authors have subsequently used the methods proposed by Hagwood to investigate DMAs operated in a wide variety of conditions including; comparison of the Knutson-Whitby equation [98] when sampling of the tail of particle distributions in the sub 5 nm range [6], Brownian motion of particles within several types of cylindrical DMA [5], determination of a simple correlation to estimate the resolution of concentric cylindrical DMAs for diffusive particles [29].

Monte Carlo modelling of particle classifiers is extremely useful in time-varying scenarios where the classifier speed or voltage is scanned i.e. varied with time. Collins et al. [34] were the first to investigate how the non-uniform gas velocity profile could affect the DMA transfer function under its scanning mode of operation. The use of Monte Carlo methods allowed for the determination of the transfer function as the scan time was reduced where an analytical expression for the particle trajectories inside the DMA was not determined at the time. They determined that the magnitude of errors in the recovered size distribution depends upon the ratio of the mean gas residence time to the exponential voltage time constant, the sheath-to-aerosol-flow ratio, and the method used to determine the delay time between the classifier outlet and particle detector.

### 2.2.5 Experimental Transfer Function Measurements

The aforementioned determination of aerosol classifiers' transfer function using analytical or Monte Carlo methods strictly encompasses the classification region. However, non-idealities can occur within actual classifiers, which include inlet and outlet sections before and after the classification section. Furthermore, classifiers may not behave exactly as predicted theoretically, and these non-idealities require experimental determination.

Quantifying the non-ideal particle behaviour within particle classifiers is typically done using tandem classification by two identical classifiers in series with one another following the work of [127], who quantified losses within DMAs. The experimentally measured tandem distribution can be compared to the theoretical convolution of the two theoretical classifier transfer functions. The theoretical transfer function can be altered with an area scaling factor and a width factor, which quantify particle loss and broadening. Johnson et al. [79] determined the experimental transfer function of the AAC using this method and found that the transmission efficiency of the AAC increases as particle size increases, ranging from 44% to 80% across its classification limits. The width of the experimental AAC transfer function was significantly broader than expected from the theory, which was postulated to be due to an adverse classifier flow effect.

Naseri et al. [133] recently determined the experimental transfer function of the CPMA through tandem classification. Evaluating the transfer function of the CPMA is somewhat more complicated than that of other classifiers owing to uncharged particle penetration and accurate knowledge of the relationship between particle charge, mass, and mobility. The width of the CPMA transfer function depends on the electrical mobility of the aerosol, as this dictates its drift across the gap. Naseri et al. [133] used an AAC to ensure that no-uncharged particles can penetrate through the CPMA. They found that the width of the triangular approximation of the CPMA transfer function was similar to theory as long as the flow rate was greater than  $0.3 \text{ L min}^{-1}$ . However, there were significant losses which were found to increase as the mass resolution of the classifier increased (which means an increase in rotational speed and voltage) and as particle mass decreased.

### 2.2.6 Data Inversion

The problem of data inversion in aerosol science can be succinctly illustrated by thinking about the convolution of the transfer functions in a system with the distribution of particles. The number of particles, typically measured by a particle counter, of a given property (such as mobility diameter, mass, or aerodynamic diameter) downstream of a classification system is given by convolving the number distribution of particles upstream of the classifier with the

whole system transfer function, often referred to as the system kernel of the instrument, which describes the probability of a particle of said property exiting the classifier. The number concentration at the  $i^{\text{th}}$  measurement point,  $N_i$ , is determined by taking the convolution of the particle number distribution and system kernel, given by

$$N_i(x_i^*) = \int K(x_i^*, x) n(x) dx + \varepsilon_i \quad (2.04)$$

where  $K(x_i^*, x)$  is the system kernel, which is the product of the individual transfer functions within the system being characterised.  $x_i^*$  defines the instrument set-point. Equation 2.04 is a Fredholm integral of the first kind and is a common problem formulation in many branches of physics and engineering. Note that for charge-based classification methods, the kernel will consist of both the classifier transfer function and the particle charge distribution for a given size.  $n(x)$  is a distribution function that describes the upstream distribution. The kernel for the unipolar charger CPMA system shown in Figure 1.3e is

$$K_i(s_i^*, m, d_m) = \sum_{q=0}^{q_{\max}} f_q(q, d_m, \mathbf{p}_i) \Omega(s_i^*, m, d_m, q, \mathbf{p}_i) \quad (2.05)$$

where  $f_q(q, d_m, \mathbf{p}_i)$  represents the fraction of particles with mobility diameter  $d_m$  that have an integer charge state  $q$ . The sum of these charge fractions for a given diameter equals one. As previously discussed, this is commonly evaluated using Fuchs' charging theory. The function  $\Omega(s_i^*, m, q, d_m, \mathbf{p}_i)$  denotes the transfer function of the CPMA at the  $i^{\text{th}}$  mass-to-charge set-point,  $s_i^*$ , which depends on the particle mass ( $m$ ), charge state ( $q$ ), and mobility diameter ( $d_m$ ). The vector  $\mathbf{p}_i$  denotes the additional operating parameters required to describe each device's transfer function. For the unipolar charger, these include ion and gas properties, particle conductivity, and the ion-concentration time product ( $n_i t$ ) of the charger. For the CPMA, relevant parameters include physical settings such as rotational speed ( $\omega$ ), voltage ( $V$ ), and aerosol flow rate ( $Q$ ), as well as gas conditions like temperature and pressure. The kernel for this system is particularly complex as the probability that a particle of a given mass transmitting through the system is not only dependent on mass but also on its mobility, diameter, and charge.

The distribution function  $n(x)$  is generally the quantity of interest for aerosol scientists. The problem of using raw measurements of concentration,  $N_i(x_i^*)$ , to obtain the actual size distribution,  $n(x)$  sampled by the instrumentation is called the aerosol inverse problem. Due to the common occurrence of this problem in aerosol science, there are several methods to tackle it. The simplest method is point-to-point inversion, used within the commercial versions of both the SMPS and AAC [79, 189]. It is assumed that the transfer function of the classifier is narrow enough that other functions, such as the counting efficiency, particle size distribution

and charging distribution, are constant over the width of the transfer function such that they can be taken out of the integral in Equation 2.04. This greatly simplifies deconvolution and is a reasonable approximation when operating classifiers with high resolution ( $R \sim 10$ ) but can become problematic for lower resolutions or for overlapping transfer functions where it is not appropriate to assume constant parameters over the transfer function width. Equation 2.04 can be discretised, leading to the following approximation

$$N_i(x_i^*) \approx \sum_{j=1}^{j=B} K_i(x_i^*, x_j) n(x_j) \Delta x_j + \epsilon_i \quad (2.06)$$

where the size distribution has been divided into  $B$  intervals. A set of  $i$  linear equations is therefore obtained. This problem can be written more succinctly as a matrix problem

$$\mathbf{A}\mathbf{x} = \mathbf{b} + \boldsymbol{\epsilon} \quad (2.07)$$

where  $\mathbf{A}$  is equal to  $K(x_i^*, x_j)\Delta x_j$  and  $\mathbf{x}$  is the discretised distribution function. The vector  $\mathbf{b}$  equal in length to the number of CPC measurements,  $\mathbf{x}$  is a  $B$  by 1 vector, and  $\mathbf{A}$  is an  $n$  by  $B$  matrix. Equation 2.07 is commonly solved using a form of least squares minimisation; however, there are a number of pitfalls and issues in solving said equation. Frequently, there are fewer measurements than unknowns in aerosol measurements, *i.e.*, the particle distribution function is often estimated at more points than the number of available measurements. As a result, the problem is underdetermined or ill-posed, and multiple solutions may exist. A variety of methods have been developed to address the challenges of inverting one-dimensional particle size distributions. These techniques are widely discussed in the aerosol literature, with numerous reviews providing valuable insights into their application and evolution. For instance, reviews by Voutilainen et al. [209] and Kandlikar and Ramachandran [88] detail methods applicable for inversion. While the complexity of the data and system transfer functions presents ongoing challenges, these reviews highlight the breadth of approaches available to tackle the problem, reflecting the continued efforts to refine and improve the accuracy of particle size distribution inversion.

## 2.3 Tandem Aerosol Classification

Through Equation 1.04, it is clear that if a pair of parameters from the trifecta of mass, aerodynamic diameter or mobility diameter are measured, the third parameter can be determined. Furthermore, other properties, such as the effective density or particle shape factor, can be derived, which provide indications of a particle's morphology. The pair-wise combina-

tions of measurements are obtained through tandem classification. Tandem classification is the process of operating two classifiers in series with one another. In tandem classification, the upstream classifier is set to a constant set-point, and the downstream classifier is stepped/scanned across its domain, followed by a particle counter, such as a CPC, used to measure the concentration as a function of the downstream classifier's changing set-point. Typically, the modal/mean value of the measured distribution is used along with the upstream classifier set-point to determine the property of interest. The modal value of the measured distribution is often obtained through fitting a Gaussian distribution in logarithmic space.

A review of measurements for particle effective density was provided by Peng et al. [154] with an even more recent review by Sipkens et al. [179] detailing tandem aerosol classification with a particular focus on soot aerosols. This section briefly details a summary of the methods used. First, it describes the methodology and calculations involved in measurements that are widely accepted as reliable [154, 179], as well as recent developments enabling faster data acquisition compared to traditional approaches.

### 2.3.1 Tandem Classification Theory

As tandem classification methods for the measurement of particle effective density are used extensively in this thesis, the theory behind the measurements is detailed herein. The definition of effective density used within this work is the ratio of the measured particle mass [42],  $m$  to the particle volume calculated using its mobility equivalent diameter,  $d_m$

$$\rho_{\text{eff}} = \frac{m}{\frac{\pi}{6} d_m^3}. \quad (2.08)$$

The mobility diameter is defined as the diameter of a spherical particle with the same electrical mobility as the particle of interest. These parameters are readily obtained from measurements of particle mass and particle mobility. However, an important distinction has to be made. A CPMA and a DMA classify particles by mass-to-charge and charge-to-drag, respectively. Therefore, the particle charge must be known to convert from these quantities to the quantities of interest (i.e., mass and mobility diameter). Other definitions of effective density detailed in DeCarlo et al. [42] use different calculation methods leading to different numerical values of effective density because they capture different particle properties. Throughout this work, Equation 2.08 is the definition of effective density used.

The charge-to-drag ratio is referred to as electrical mobility, which is defined as the velocity of a charged particle per unit electric field strength [70] and is given by

$$Z_p = \frac{V_T}{E} \quad (2.09)$$

where  $V_T$  is the terminal velocity of the particle due to the electrostatic field  $E$ . The DMA classifies particles by balancing the electrostatic and drag force on a particle. The mobility equivalent diameter can be derived from the electrical mobility by inverting the following relationship [42]

$$Z_p = \frac{qeC_c(d_m)}{3\pi\mu d_m} \quad (2.10)$$

where  $e$  is the elementary charge,  $q$  is the number of elementary charges on the particle,  $C_c$  is the Cunningham slip correction factor and  $\mu$  is the gas viscosity. The knowledge of the particle charge state is extremely important in obtaining accurate measurements of effective density using Equation 2.08. Non-spherical particles can cause issues in the ability to discern multiple charging peaks in measured spectra [160], leading to measurement errors.

As previously mentioned, the AAC classifies particles by their mass-to-drag ratio by balancing a centrifugal force to a drag force thereby classifying particles based on their relaxation time,  $\tau$ . The particle relaxation time, which is the characteristic time of a particle to respond to a change in applied force, is defined as the product of particle mass and mobility

$$\tau = mB. \quad (2.11)$$

The particle mobility,  $B$  is the constant of proportionality relating the drag force,  $F_D$  on a particle to the terminal velocity of a particle

$$B = \frac{V_T}{F_D}, \quad (2.12)$$

The mobility of a particle is related to its electrical mobility through

$$B = \frac{Z_p}{qe}. \quad (2.13)$$

By combining Equations 2.13 and 2.08 the particle relaxation time can be expressed in terms of the particle effective density and particle mobility diameter as

$$\tau = \frac{\rho_{\text{eff}} d_m^2 C_c(d_m)}{18\mu}. \quad (2.14)$$

The particle relaxation time can also be expressed in terms of an aerodynamic diameter, which is defined as a spherical particle of unit density ( $\rho_0 = 1000 \text{ kg m}^{-3}$ ), which has the same settling velocity as the particle of interest:

$$\tau = \frac{\rho_0 d_a^2 C_c(d_a)}{18\mu}. \quad (2.15)$$

Combining Equations 2.14 and 2.15 yields an expression for the particle effective density in terms of mobility and aerodynamic diameter

$$\rho_{\text{eff}} = \frac{\rho_0 d_a^2 C_c(d_a)}{d_m^2 C_c(d_m)} \quad (2.16)$$

which can be obtained from tandem measurements using an AAC and DMA [195].

Throughout this work, Cunningham slip correction and air viscosity are taken from the empirical work of Kim et al. [93]. The Cunningham slip correction factor can be estimated from the following correlation:

$$C_c(d_m) = 1 + \frac{\lambda}{d_m} \left( \alpha_c + \beta_c \exp\left(\frac{-\gamma_c d_m}{\lambda}\right) \right) \quad (2.17)$$

where  $\alpha_c = 2.33$ ,  $\beta_c = 0.966$  and  $\gamma_c = 0.4985$ . The mean free path,  $\lambda$  and viscosity  $\mu$  of the surrounding gas can also be estimated from the same source [93]:

$$\lambda = \lambda_0 \left( \frac{T}{T_0} \right)^2 \left( \frac{P_0}{P} \right) \left( \frac{T_0 + S}{T + S} \right) \quad (2.18)$$

and

$$\mu = \mu_0 \left( \frac{T}{T_0} \right)^{\frac{3}{2}} \left( \frac{T_0 + S}{T + S} \right) \quad (2.19)$$

where  $\lambda_0$  reference value of the air mean free path taken as 67.3 nm,  $\mu_0$  is the air viscosity reference given by  $1.83245 \times 10^{-5}$  Pa s,  $T$  is the air temperature in the classifier,  $T_0$  is the reference temperature of 296.15 K,  $P$  is the air pressure in the classifier,  $P_0$  is the reference pressure of 101325 Pa and  $S$  is the Sutherland constant for air which is 110.4 K.

After measurement, obtaining empirical parameters to relate the particle mass to mobility is common. This relation is typically given by

$$m = k d_m^{D_m} \quad (2.20)$$

Where  $k$  and  $D_m$  are referred to as the mass mobility pre-factor and mass mobility exponent, respectively. This equation can also be phrased in terms of particle effective density [128]

$$\rho_{\text{eff}} = \frac{6}{\pi} k d_m^{D_m-3} = \rho_{\text{eff},100} \left( \frac{d_m}{100 \text{ nm}} \right)^{D_m-3}, \quad (2.21)$$

which is often anchored to a physical value of effective density, typically, the effective density of a 100 nm particle,  $\rho_{\text{eff},100}$  [147]. Therefore, in literature, it is common to see values of  $k$ ,  $\rho_{\text{eff},100}$  and  $D_m$  to describe the mass-mobility relation of an aerosol.

### 2.3.2 Tandem DMA, CPMA and AAC measurements

Typical tandem measurements combine any two of a DMA, AAC or PMA. As these three devices measure different aerosol properties, namely electrical mobility, relaxation time, and mass-to-charge ratio, tandem combinations allow further characterisation of an aerosol by determining its effective density and shape factor. The DMA-PMA system was first used by McMurry [128] and Ehara and Shin [46] to measure spherical particles as well as those emitted from atmospheric sources. As of 2021, this technique has been used in approximately 50 studies investigating a wide variety of different aerosols as summarised by Peng et al. [154].

Measurements of  $d_m$  and  $d_a$  can also be combined in a similar manner. This approach using the AAC-DMA was proposed by Tavakoli and Olfert [195] and used to measure the density of Di-octyl Sebacate (DOS) and soot particles. Due to the relative infancy of the AAC compared to both the DMA and PMAs, this tandem technique is slightly less common in the literature. However, it has been used to measure particle mixing state [208] and effective density of ambient aerosols in Beijing [115]. This technique offers considerable benefit in the identification of multiple charge peaks and can even be used to determine particle charge distributions [80, 81].

The final combination is the AAC-CPMA, which is not particularly prominent in the literature. Both Kazemimanesh et al. [89] and Yao et al. [224] have used all three different pairwise measurements for a Gasoline Engine and Ammonium Sulphate, respectively. It was found that the AAC-CPMA was more erroneous than the other two methods. This is confirmed by error propagation, which takes into account errors in individual parameters and assumes independence. Authors have reported the uncertainty in measurement effective density to be 9.4%, 11.1% and 28.4% for the DMA-CPMA, AAC-DMA and AAC-CPMA respectively [89].

It should be noted that using tandem methods strictly provides a measurement of the average quantity of interest. All classifiers select particles of an average value of the respective particle property because the transfer functions have finite widths. Classifier set points are, therefore, considered averages over the sampled population. Furthermore, it is common

practice to take either the modal value of the measured downstream distribution or fit a Gaussian distribution to the data from which the peak value is extracted. This modal or peak value, along with the upstream classifier set-point, is then used in the subsequent analysis described in section 2.3.1. Therefore, all parameters, such as effective density and shape factor are averages of the classified particle population.

### 2.3.3 Tandem Measurements to determine mass distributions

Distribution measurements made with a single classifier can be readily converted to other distributions if the size-dependent particle density is known. This is straightforward if the particles are spherical and the particles are of a known density [79]. However, if the particle density varies as a function of size, then knowledge of this dependency is required, either through prior measurement of the effective density or the use of literature values, to convert from different quantities as detailed in Section 2.3.1. If constant values are used, conversion between different particle size distributions becomes erroneous. Therefore, one solution to determining mass distributions, allowing for measurement of total mass concentrations, is prior measurement of the mass-mobility relation, in which a PMA is paired with a DMA to determine the average mass of particles with a specific value of mobility diameter (*i.e.* the mass-mobility relation). Park et al. [152] measured the mass per particle as a function of mobility size,  $m(d_m)$  using a tandem DMA-APM-CPC system followed by measurements of the number weighted mobility diameter distribution,  $\frac{dN}{d\log d_m}$  using an SMPS. Multiplying the mass per particle by the number distribution provides a mass-weighted particle size distribution

$$\frac{dM}{d\log d_m} = m(d_m) \frac{dN}{d\log d_m}. \quad (2.22)$$

Equation 2.22 can be integrated to determine the particle mass concentration. They found this method for determining mass concentration accurate to within 20% compared to gravimetric analysis for a range of aerosols. The main downside to this method is the requirement for a previous measurement of  $m(d_m)$ , which is often time-consuming and not feasible in some experimental scenarios. In this case, uncertainty may also be introduced by extrapolating previously measured mass-mobility relationships to new measurements if they are not performed sequentially. Furthermore, the DMA is limited to measuring particles less than  $<\sim 600$  nm, which might significantly truncate a mass-weighted distribution.

Various other combinations of single distribution measurements combined with measurements/assumptions of particle effective density relations have also been implemented to measure both mass distribution and mass concentrations. Peters et al. [156] compared distributions obtained from a differential mobility particle sizer (DMPS) or an electrical

aerosol analyzer (EAA) with an aerodynamic particle sizer (APS) to measure the number distributions of NaCl aerosols. To obtain mass distributions, they assumed particles were cubic, with a density equal to the bulk density of NaCl. Maricq and Xu [124] combined a DMA and ELPI to measure the effective density of soot particles. It was proposed that, theoretically, integrated particle mass concentrations can be determined from ELPI measurements to within 25% by making assumptions about the width of the measured size distribution and fractal dimensions of the particle. They confirmed this experimentally in future work, demonstrating that due to the negative correlation between the determination of particle concentration and mobility diameter, the proposed technique had only a weak dependence on particle effective density [122].

### 2.3.4 Increased measurement speed for tandem classification

Stepping or scanning the downstream classifier during tandem classification can take significant time, ranging from 2 - 20 minutes, depending on the experimental configuration. This significantly increases experimental time and limits the applicability of tandem classification for real-time process monitoring. Many authors have demonstrated ways to increase the speed of effective density measurements, which are discussed in the following section.

Initially, the DMA-CPMA/APM-CPC set-up was reversed such that particles are first selected by their mass-to-charge ratio, and then the DMA is scanned to obtain a mobility distribution [120]. Scanning a DMA is significantly faster ( $\sim 2 - 3$  minutes) than stepping a mass analyser ( $\sim 10 - 20$  minutes) due to the acceleration required to rotate the cylinders of the classifier. Although significantly quicker, this reversed method does not provide a real-time measurement of effective density. Tandem configurations utilising fast particle sizers such as the Electrical Low Pressure Impactor (ELPI) or Differential Mobility Spectrometer 500 (DMS500) have been employed to facilitate faster size-resolved effective density measurements owing to the sub 1 second time resolution of such instruments. A tandem system combining a DMA with an ELPI has been used to measure the effective density of a wide range of aerosols [43, 124, 12, 164]. One of the main drawbacks of the TDMA-ELPI set-up is the presence of multiply charged particles downstream of the DMA, which have to be accounted for to minimise any skewing in effective density measurements [43, 124]. Johnson et al. [84] paired a CPMA and DMS-500 to measure particle effective density. Once size calibrated and corrected for multiple charge artefacts, the unipolarly charged CPMA-DMS was shown to measure the effective density of DEHS within 12.6% with a bias uncertainty of 30.6%. The fast response of the DMS relative to a DMA allowed for transient measurements of the particle effective density of cigarette smoke [82]. However, the CPMA-DMS pairing was only demonstrated over a narrow size range (100 - 300 nm).

Modifications to commonly used tandem configurations have been made to further increase the measurement speeds of effective density to near real-time acquisition. Rostedt et al. [166] and Juuti et al. [86] paired a zeroth order mobility analyser with an ELPI to measure both mobility and aerodynamic diameter in real-time, which allowed for an estimate of the average effective density of the aerosol. However, this technique does not provide a size-resolved measurement but rather an average over the whole aerosol population, which is not an accurate measure for aggregated particles whose effective density decreases as their mobility diameter increases.

### 2.3.5 Two-Dimensional Distribution Inversion

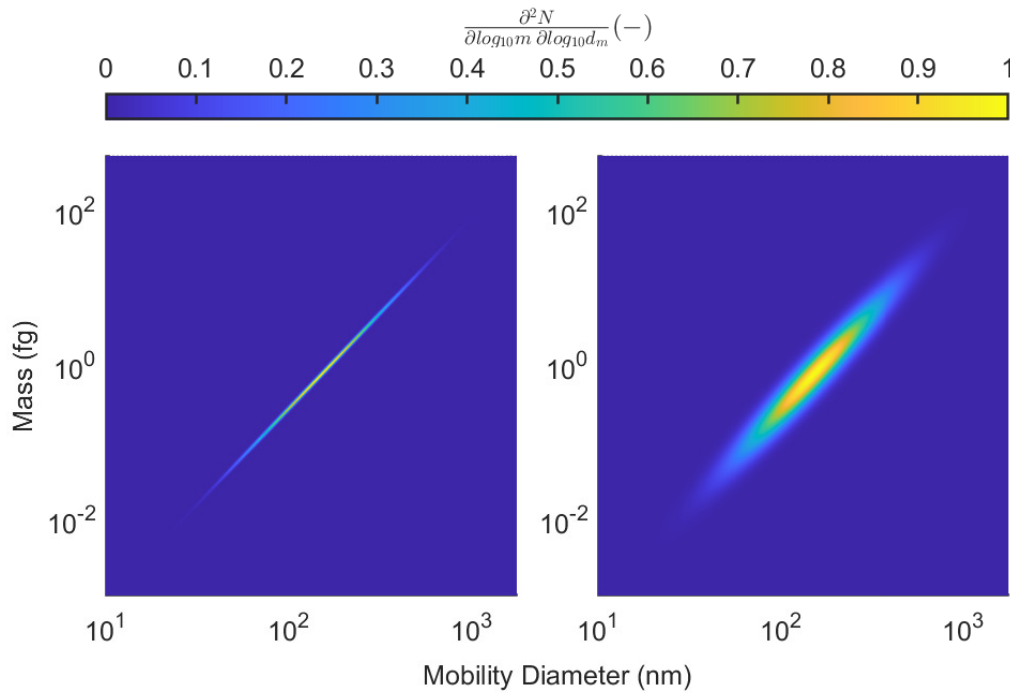


Fig. 2.2 Example theoretical two-dimensional distributions in mass-mobility space. The figure on the left represents a narrow distribution that would be obtained from an aerosol with a narrow range of morphologies. In contrast, the figure on the right represents a distribution with a wide range of particle morphologies.

It should be reiterated that the aforementioned literature regarding conventional tandem methods, in which either peak finding or Gaussian fitting finds the modal value of the measured downstream distribution, strictly provides an average measurement of the downstream distribution. Consequently, any further parameters determined in this manner, such as particle effective density or shape factor, are also average quantities. These methods, therefore, fail to

describe the distribution of properties that exist in an aerosol population. More recent work has demonstrated that a more complete understanding of the two-dimensional relationship between quantities can be obtained by determining two-dimensional distributions. The experimental setup for determining such two-dimensional distributions is identical to a conventional tandem measurement. However, the data can be inverted using different techniques rather than going down the traditional analysis routes. These techniques, therefore, enable the reconstruction of full two-dimensional mass- mobility distributions rather than the average quantities prescribed by conventional analysis. This methodology is particularly powerful for agglomerate structures with a distribution of particle masses at each mobility diameter owing to the variety in shape and structure exhibited by agglomerates.

The technique of two-dimensional inversion was first introduced by Rawat et al. [161] for a tandem DMA-APM set-up. Rather than solving for a one-dimensional distribution in a single property space as given by Equation 2.04, the convolution can be extended to include a tandem classification system. Using the example of a tandem CPMA-DMA system, the number concentration at a given DMA set-point ( $i$ ) and CPMA set-point ( $j$ ) is given by

$$N_{i,j} = \int_0^\infty \int_0^\infty \sum_{q=0}^{q=\infty} f_q(q, d_m) \Omega_i(d_m, q) \Lambda_j(m, d_m, q) \frac{\partial^2 N}{\partial \log d_m \partial \log m} d \log d_m d \log m + \epsilon_i, \quad (2.23)$$

where  $\partial^2 N / \partial \log d_m \partial \log m$  is the number-based two-dimensional mass-mobility distribution,  $\Omega_i(d_m, q)$  and  $\Lambda_j(m, d_m, q)$  are the transfer functions of the DMA and CPMA, respectively and  $f_q(q, d_m)$  is the charge fraction of particles with  $q$  elementary charges of diameter  $d_m$ . Single property distributions, sometimes referred to as marginal distributions, such as number-weighted mass and mobility distributions (*e.g.*,  $dN/d \log d_m$  and  $dN/d \log m$ ) can readily be obtained by integration over a single property domain. Example theoretical two dimensional distributions are shown in Figure 2.2. The figure on the left represents a narrow distribution which would be obtained from an aerosol with a narrow range of morphologies *e.g.* compact/spherical particles. The figure on the right represents a distribution with a range of particle morphologies more akin to a soot aerosol, where a distribution of particle masses exists at a given mobility diameter. Figure 2.2 highlights the potential power of two-dimensional inversion procedures as it elucidates the range of given properties at a given particle, not just the average of the given properties.

Rawat et al. [161] measured two-dimensional distribution reconstructions for salt aerosols, soot and externally mixed ammonium sulphate and soot. They demonstrated that all three salt aerosols form particles with effective densities close to their bulk values, which indicates the formation of particles with a compact structure. On the other hand, soot aggregates produce

a broad range of masses at each particle mobility diameter, indicating a variety of particle morphologies with the same mobility diameter. Rawat et al. [161] therefore argued that the use of single-valued mass-mobility relations does not fully characterise soot aerosols due to the wide range of morphologies present in the population. Buckley et al. [22] improved on the inversion algorithm presented by Rawat et al. [161], making it conditionally stable for a wider range of operating conditions.

More recently, Sipkens et al. [181] provided a comprehensive review of inversion techniques for two-dimensional distribution inversion. The same authors then extended this analysis to include novel Bayesian Approaches [178]. The techniques described by Sipkens have been implemented in different experimental settings. Trivanovic et al. [202] measured the mass-mobility distributions of a wide range of fuels. They demonstrated that the width of the conditional mass distribution, that is, the width of the mass distribution at a given mobility diameter, found by fitting bivariate log-normal distributions to the inverted data, was between 1.28 - 1.40. A compact aerosol is likely to have a width between 1 - 1.1 (i.e. the mass-mobility relation is close to single-valued), conditional widths greater than this indicate a variety of structures exist at a given mobility diameter. It was also found that the width of the conditional distributions increased with increasing mass and mobility diameter. Sipkens et al. [183] then utilised the methods to measure the mass-mobility distribution of externally mixed salt and soot particles. SMPS measurements alone could not distinguish the two-particle modes of salt and soot at higher salt concentrations. However, two-dimensional mass-mobility distributions enabled the characterisation of distinct modes, revealing mostly distinct soot and salt modes.

Two-dimensional inversion has also been applied to tandem techniques other than the CPMA-SMPS. Broda et al. [21] combined a CPMA and a Single Particle Soot Photometer (SP2) to measure the refractory black carbon mass as a function of particle mass. Morán et al. [131] characterised the two-dimensional size and charge distribution of particles sampled from an electrostatic precipitator using a tandem DMA-DMA and DMA-Aerodynamic Particle Sizer (APS).

It should be noted that when sampling an aerosol, the underlying population always has a distribution of quantities. The width of this distribution will depend on the type of particles present. This, therefore, may impact inversion when measuring with single classifiers, as it is typical to assume single-valued functions for mass, mobility, and particle charging when calculating the inversion kernel, which may lead to inaccurate distribution determination.

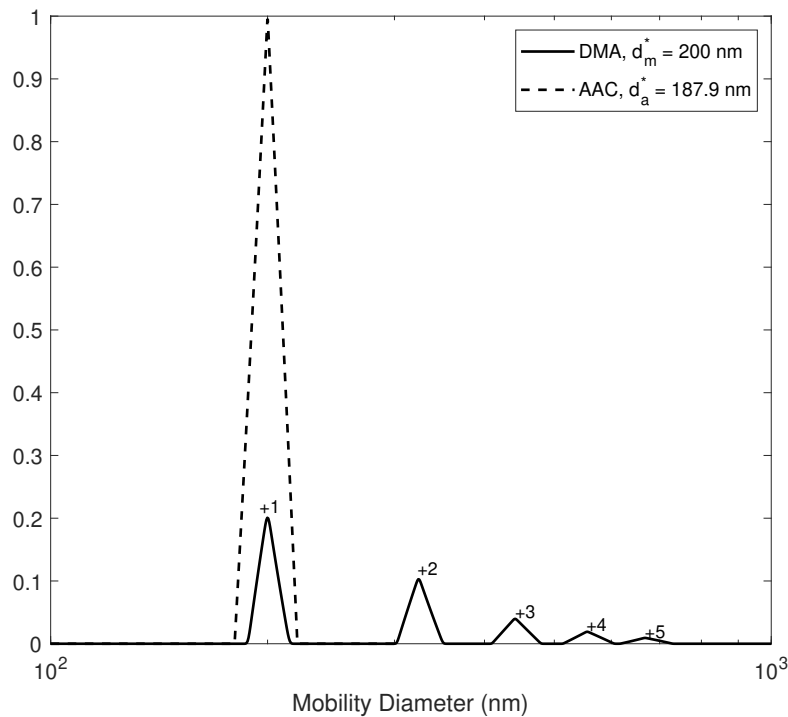


Fig. 2.3 Removal of multiply charged particles through tandem classification. The tandem operation of an AAC-DMA ensures that only singly charged particles exist in the measured population. In this example, the AAC is set to an aerodynamic diameter of 187.9 nm and the DMA set to a mobility diameter of 200 nm to account for the density of the particle, taken as  $913 \text{ kg m}^{-3}$ .

### 2.3.6 Generating Singly Charged Particles

The final application of tandem classification, which is beneficial in instrument calibration, is the generation of particles with a known charge state. This is particularly important regarding the calibration of CPCs with electrometers, which are extensively used in this work. The most reliable method of generating a population of singly charged aerosols is tandem classification, illustrated in Figure 2.3 for the tandem combination of an AAC and DMA. For a particle with a known mass-mobility relation (*e.g.* spherical particles) Song et al. [184] demonstrated that the resolutions of any pair-wise combination of an AAC, DMA and CPMA can be constrained to guarantee that only singly charged particles exit the downstream classifier. This technique has been used for calibration of CPCs [151] over a wide particle size range. Compared to other methodologies, the benefit of this method is the lack of requirements to correct for multiple charging artefacts, which can increase uncertainty in calibration.

## 2.4 Objectives

The overall objectives of this work can be divided into two categories. The first revolves around understanding the effect of humidity on charging-based measurements, and the second involves developing unipolar charger-particle mass analyser systems with the main aim of providing measurement of particle mass distributions and particle morphology.

1. Investigate the response of three commonly used charging techniques as relative humidity varies. This can be further separated into
  - (a) Measurement of the Ion-Mobility Distributions of unipolar and bipolar chargers as a function of relative humidity using a High-Resolution DMA
  - (b) Measure the mean charge per particle as a function of humidity for three commonly used charging methods, namely, unipolar, bipolar and photoelectric charging
2. Development and advancement of methods utilising unipolar-charger-CPMA systems
  - (a) Experimental validation of methods to determine the average mass transmitted through unipolar-CPMA systems
  - (b) Characterisation of a new particle classifier, the Mobility Separator Electrometer (MSE), through numerical modelling and experimentation
    - i. Numerical derivation and the experimental validation of the classifier transfer function
    - ii. Numerical modelling to assess tandem measurements using an AAC/CPMA, Unipolar Diffusion Charger, MSE and CPC, enabling measurement of particle effective density
    - iii. Experimental validation of effective density measurements
  - (c) Determination of mass distributions using unipolar charger-CPMA systems.
    - i. Utilise a numerical model to highlight the potential pitfalls of using a unipolar charger-CPMA system to determine particle mass distributions
    - ii. Introduce a new measurement system, the Mass Mobility Aerosol Spectrometer ( $M^2AS$ ), which utilises the MSE to provide additional measurement, enabling accurate mass distribution determination.
  - (d) Experimental Validation of the  $M^2AS$  System, which is further split into three sub-objectives

- 
- i. Validation of the M<sup>2</sup>AS effective density measurement using spherical/compact aerosols
  - ii. Validation of the M<sup>2</sup>AS effective density measurement of non-spherical particles by comparison to a CPMA-SMPS system
  - iii. Validation of size distribution measurements from the M<sup>2</sup>AS through comparison to SMPS measurements for both spherical/compact and non-spherical aerosols



## Chapter 3

# Experimental Investigation of the effect of Relative Humidity on Particle Charging

### 3.1 Introduction

As particle charging is so ubiquitously used for aerosol measurements in ambient environments, an assessment of the impact of water vapour concentration on charging is essential. Charging sensors used in ambient environments are typically calibrated in laboratory conditions with dry air ( $RH \leq 10\%$ ) but then subsequently used in environments in which the humidity may be significantly higher and further vary through a measurement campaign. This chapter investigates the potential influence of humidity on commonly used particle charging techniques, including bipolar and unipolar diffusion charging and direct ultra-violet photoionisation, through experimentation. A HRDMA was used to measure the ion electrical mobility distributions for three different diffusion chargers as RH was varied. As ion properties, namely mass, mobility and concentration, dictate the charging process, direct measurement of charging ions can elucidate the effect of humidity without viewing charging as a black box. A second series of experiments measured the mean charge per particle acquired by a monodisperse aerosol for both unipolar and bipolar diffusion chargers as well as a photoelectric charger as a function of RH.

### 3.2 Measurement Principles: Mean Charge

#### 3.2.1 Bipolar Diffusion Chargers

Within a bipolar charger, gas molecules are ionised using radiation, X-rays or corona discharge in such a manner as to produce both positive and negative ions. Ions then transfer their

charge to nearby particles due to diffusive and electrostatic forces. Given a sufficiently high ion concentration and residence time within the charger, a steady state charge distribution is reached wherein the charge distribution is only a function of the particle size and ionic properties. Within low-cost sensors, the measured net current or mean aerosol charge is related to the properties of the aerosol size distribution. A simplified approximation for the mean charge  $\bar{q}_d$  of a monodisperse aerosol at bipolar charge equilibrium is given by [141, 33]

$$\bar{q}_d = \frac{2\pi\epsilon_0 k_b T}{e^2} \ln \left( \frac{Z_+}{Z_-} \right) d \quad (3.01)$$

where  $\epsilon_0$  is the vacuum permittivity,  $k_b$  is Boltzmann's constant,  $T$  the carrier gas temperature,  $e$  the electron charge,  $d$  is the particle diameter and  $\frac{Z_+}{Z_-}$  the ion mobility ratio. It is clear from this approximation that for a monodisperse particle distribution at a constant gas temperature, the mean charge on the particle is only dependent on the ion mobility ratio<sup>1</sup>. Nishida et al. [141] demonstrated Equation 3.01 holds for sizes between 50 - 1000 nm and can be used to approximate the average ion-mobility ratio of the charger being investigated.

### 3.2.2 Unipolar Diffusion Chargers

Unipolar charging produces a high flux of positive or negative ions which diffuse towards the particle, leading to high particle charge levels. A simple model for the mean charge of unipolar charged aerosol was determined by White [217]:

$$\bar{q} = \frac{dk_b T}{2K_E e^2} \ln \left( 1 + \frac{\pi d \bar{K}_E \bar{c}_i e^2 n_i t}{2k_b T} \right) \quad (3.02)$$

where  $K_E = 1/(4\pi\epsilon_0)$  and  $\bar{c}_i$  is the mean thermal speed of the ions.  $n_i t$  is the ion-concentration residence time product. White's equation elucidates essential parameters governing unipolar charging dynamics, but its applicability is confined to the continuum regime due to omitting image charge effects [50]. Fuchs [49] derived a more commonly used model to determine the charge distribution in which a limiting sphere approach is applied to determine the ion-aerosol attachment coefficients within the transition regime. Ions inside the limiting sphere are assumed not to collide with the gas molecules (free molecular conditions), while ions outside of the limiting sphere are assumed to follow the diffusion-mobility equation for a continuum. These two regimes are then coupled by matching the flux at the limiting sphere radius around the particle. Due to the complexity of Fuchs' charging model, and extensive experimental observation, it is common to approximate the average charge with a power law:

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<sup>1</sup>Assuming that the charging process has reached a steady state and the number concentration of positive and negative ions are equal

$$\bar{q}_d = q_0 d^\nu \quad (3.03)$$

For aerosols within the transition regime, the exponent,  $\nu$ , is typically between 1.1 and 1.3 [85, 13, 14, 199, 125, 199]. However, the exponent can be larger than this in direct chargers where the aerosol is subject to high electric fields, which can lead to significant particle loss [150]. In the context of portable sensors, the response of diffusion charging sensors is often conflated as Lung Deposited Surface Area Concentration (LDSA) because the charging efficiency and the LDSA per particle share approximately the same size dependence in a size range from approximately 20 nm to 400 nm.

### 3.2.3 Photoelectric Chargers

Unlike diffusion chargers, photocharging directly charges the aerosol using UV light. If the irradiation intensity is sufficient to overcome the material's work function, a particle will emit an electron, resulting in a positively charged particle. The mean charge of a monodisperse aerosol in a photoelectric charger where ion-particle recombination is limited is given by [137]

$$\bar{q}_d = \frac{I}{4h\nu} t_{\text{irr}} Y \bar{\sigma}_{\text{ph}} = c d_m^x. \quad (3.04)$$

where  $I$  is the irradiation intensity,  $h\nu$  is the photon's energy,  $Y$  is the quantum yield per incident photon,  $t_{\text{irr}}$  is the irradiation time and  $\bar{\sigma}_{\text{ph}}$  is the photoelectrically active surface area. For monodisperse spheres of homogeneous material, assuming photoemission takes place over the whole particle surface area,  $\bar{\sigma}_{\text{ph}} = \pi d_p^2 = \pi d_m^2$ . Therefore, the mean charge on an aerosol with a homogeneous surface is proportional to the surface area of the particle, such that the exponent  $x$  is approximately equal to 2. Nishida et al. [136] demonstrated that this is the case for both soot and silver particles. However, the constant  $c$  varies with particle morphology and material.

## 3.3 Experimental Method

### 3.3.1 Mean Charge Measurements

The aerosol generation, conditioning and measurement of mean charge are shown in Figure 3.1. To test both unipolar and bipolar diffusion charging Bis(2-ethylhexyl) sebacate (DOS) particles were generated using a BGI Collison nebuliser. A liquid trap was placed downstream of the nebuliser to capture excess fluid mobilized during atomisation. Due to DOS's weak

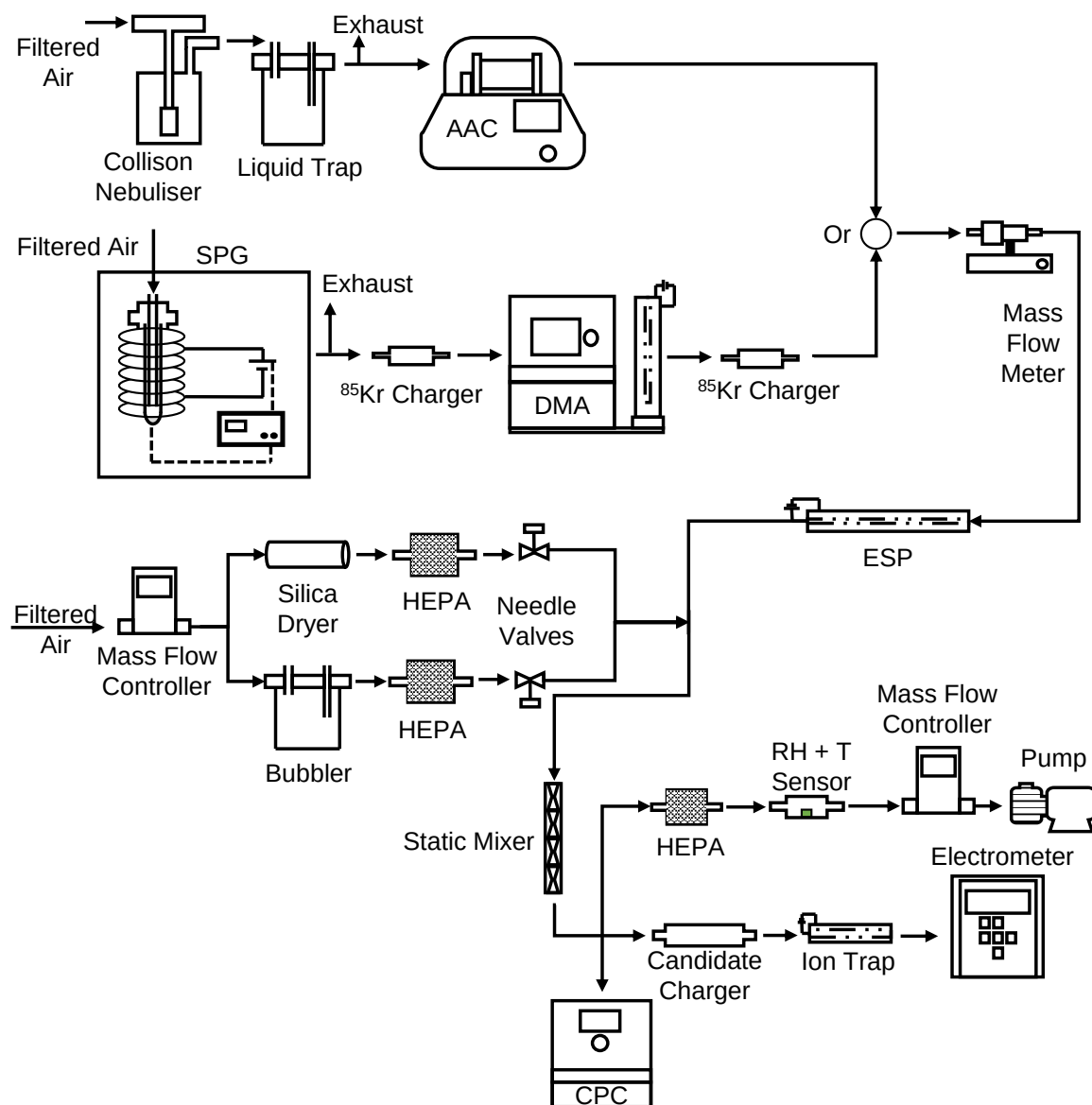


Fig. 3.1 Schematic demonstrating the generation and size selection of a monodisperse, neutral humidity-controlled aerosol stream to evaluate the mean charge per particle for a candidate charger as a function of relative humidity.

response to UV light, a different aerosol source was required to test the photoelectric charger. Here, Silver particles were generated using the Silver Particle Generator (SPG, Catalytic Instruments) in mode two without dilution flow. The SPG is a vertical tube furnace containing a reservoir of solid silver, which is heated to produce a vapour that condenses into nanoparticles in a controlled carrier gas flow, described in detail by [64].

Depending on the charging method investigated, two different classification methods were used. For the diffusion chargers, particles were classified by an Aerodynamic Aerosol Classifier (AAC; Cambustion Ltd., Cambridge, UK) to generate an aerodynamically monodisperse source. As DOS produces spherical particles, the aerodynamic diameter can be converted to a mobility diameter using the bulk density of the material, which is  $913 \text{ kg m}^{-3}$ . The mobility diameter is the equivalent diameter of choice commonly used to validate bipolar and unipolar diffusion charging theory [141, 80, 81]. The AAC was operated with balanced flows at a sheath-to-aerosol ratio of 10. The aerosol flow through the AAC was measured downstream of the AAC using an aerosol mass flow meter (Aerosol Flow Meter Accessory; Cambustion Ltd., Cambridge, UK). A custom-built electrostatic precipitator (ESP), operated at 1 kV (Electric field of  $\sim 70 \text{ kV m}^{-1}$ ), removed any charged particles created during the atomisation process, as confirmed using an aerosol electrometer (TSI Inc., Shoreview, MN, USA: Model 3068B). For the photocharger the AAC was not used as the particles produced in mode 2 operation are non-spherical [64], which makes converting between aerodynamic and mobility diameter difficult without additional measurement. Therefore, silver particles for the photocharger's characterisation were selected based on mobility diameter with a DMA. As all particles that exit the DMA are charged, an additional bipolar charger followed by an ESP was used downstream of the DMA to ensure only neutral particles existed within the sample. The DMA was operated with balanced flows at a sheath-to-aerosol ratio of 10. The classified neutral aerosol was then mixed with a combination of dry air, produced by passing HEPA-filtered compressed air through a diffusion dryer filled with silica desiccant beads (Scientific Laboratory Supplies Ltd.) followed by a HEPA filter, and humid air generated by bubbling compressed air through a glass vessel containing De-Ionised water (Scientific Laboratory Supplies Ltd.) which was then subsequently passed through a HEPA filter. The humidity was altered by changing two needle valves. The monodisperse aerosol flow and humidified air were mixed in a static mixer to ensure uniform conditions for sampling. To balance the flows between the sampling instrumentation and the additional humidified flow and ensure that the sample was drawn through either the AAC or DMA, the additional flow was pulled through a HEPA filter via a mass flow controller and pump. The relative humidity and temperature were measured in this flow line using two RH and Temperature sensors (Sensirion SHT85), with a reported RH accuracy of  $\pm 3\%$  between 1 and 85% RH. After generation, classification and humidification, the aerosol was sampled to determine the particle charge as a function of humidity.

As previously described, the charging process for all three aforementioned charging methods applied in continuous flow devices can be characterised by determining the average number,  $\bar{q}$ , of elementary charges,  $e$ , carried by monodisperse particles. This is done by

simultaneously measuring the particle number concentration  $N$  and the electrical current,  $i$  of particles deposited within a Faraday cage, operating at a flow rate  $Q$  using an aerosol electrometer. The following equation can then determine the mean charge,

$$\bar{q} = \frac{i}{NeQ}. \quad (3.05)$$

The number concentration upstream of the candidate charger was measured using a Condensation Particle Counter (TSI, Model 3752) operating at  $1.5 \text{ L min}^{-1}$ . Three different charging mechanisms were investigated using different types of chargers. A brief description of each charger is provided.

The unipolar charger investigated was the original charging module of an ELPI, which is a needle-based corona charger [150]. The ELPI charging module was operated using the ELPI high-voltage power supply, which is current-controlled. The current is maintained at  $1 \mu\text{A}$ , and the voltage can vary to maintain this value. Initially, the CPC was placed upstream of the ELPI charging module and the electrometer downstream. However, as the voltage varied to maintain a constant current, the losses within the charger would also vary, meaning only the electrometer was sensitive to this. Therefore, the CPC was placed downstream of the ELPI as well (not shown in Figure 3.1). Thus, the mean charge measurement were not affected by variations in voltage. Both the electrometer (TSI Inc., Shoreview, MN, USA: Model 3068B) and the CPC pulled a sample flow of  $1.5 \text{ L min}^{-1}$  through the charger, providing a total of  $3 \text{ L min}^{-1}$  through the charger.

The photocharger used was the same as developed and validated by Nishida et al. [139]. The chamber consists of two coaxial stainless steel electrodes. A UV-extended fused silica optical window of 25 mm diameter and 3 mm thickness (UQG Optics Ltd, Cambridge) was used to introduce UV light into the stainless steel chamber. A 3 W UV lamp (Dinies Technologies GmbH, Germany: Model Mini3W-52ozon) was located externally, 20 mm from the window. The UV source and window are located nearest the sample inlet so that the flow direction is away from the light source. A constant voltage of 30 V was applied to the centre electrode to minimise ion-particle recombination and remove excess ions. The electrometer controlled the flow through the photocharging chamber to  $1.5 \text{ L min}^{-1}$ .

The final charger investigated was a Kr-85 source (TSI Inc.: Model 3088) through which  $1 \text{ L min}^{-1}$  of flow was pulled. An electrostatic precipitator (ESP; Cambustion Ltd., Cambridge, UK) was operated at 5 V to remove ions convected with the flow (but not remove any charged particles), which could not only interfere with the electrometer measurement but also alter the charge distribution downstream of the charger [3, 80]. Ideally, ions would be immediately removed upon exit from the charger to prevent downstream charging completely;

however, due to experimental constraints, the charger outlet was connected to the inlet of the ESP via a 10 cm piece of tubing.

After adjusting the relative humidity, a minimum of 10 minutes was allowed for the relative humidity within the charger to purge and equilibrate. Subsequently, both number concentration and current were measured over a 90 s period with a 1 Hz sampling frequency. This was repeated for five different particle sizes at each humidity point. Due to the absence of a temperature-controlled laboratory environment, fluctuations in ambient temperature occurred throughout these experiments due to varying outside temperatures and heat generation from other equipment used within the shared laboratory space. During the experiments room temperatures ranged between 21 °C and 25 °C. Consequently, when comparing data which was taken separately, e.g. ion mobility measurements (Section 3.3.4) and mean charge measurements discussed in Section 3.4.3, the measured relative humidity and temperature data is converted into a water vapour concentration in parts per million on a volume basis versus the amount of dry air.

### 3.3.2 The effect of humidity on electrometer-CPC measurements

A note has to be made on the electrometer's sensitivity to relative humidity changes. J-Fatokun et al. [75] demonstrated experimentally that electrometers can be sensitive to changes in humidity such that inaccuracies in current measurements can occur, attributed to the drift of the zero offset. Their work exposed the whole electrometer (TSI Model 3068A) to a humid environment. In contrast, the electrometer circuitry in this work was not exposed to the high humidity conditions, as the flow path is sealed from the circuitry and vented off to exhaust. However, the effect of humidity on the TSI 3068B electrometer was still evaluated by measuring the charge per particle for a singly charged aerosol generated using a tandem AAC-DMA [184]. The combination of an AAC and DMA ensures only singly charged particles exist within the sample, enabling calibration of the counting ratio of the CPC to the electrometer. The calibration results are shown in Figure 3.2, which displays the charge per particle as a function of relative humidity. The average charge per particle is slightly lower for humid conditions than dry conditions, with a maximum difference between calibration values at dry ( $\sim 7\%$ ) and humid ( $\sim 80\%$ ) of 4.4%. It should also be noted that there was no visible drift in the measurement over 20 minutes, and no hysteresis was observed going from humid to dry conditions, as demonstrated by a comparison of the two data points at  $\sim 7\%$  RH, which were taken before and after humidification took place. The zero offset was also evaluated and found to drift by less than 1 fA throughout the measurements shown in Figure 3.2.

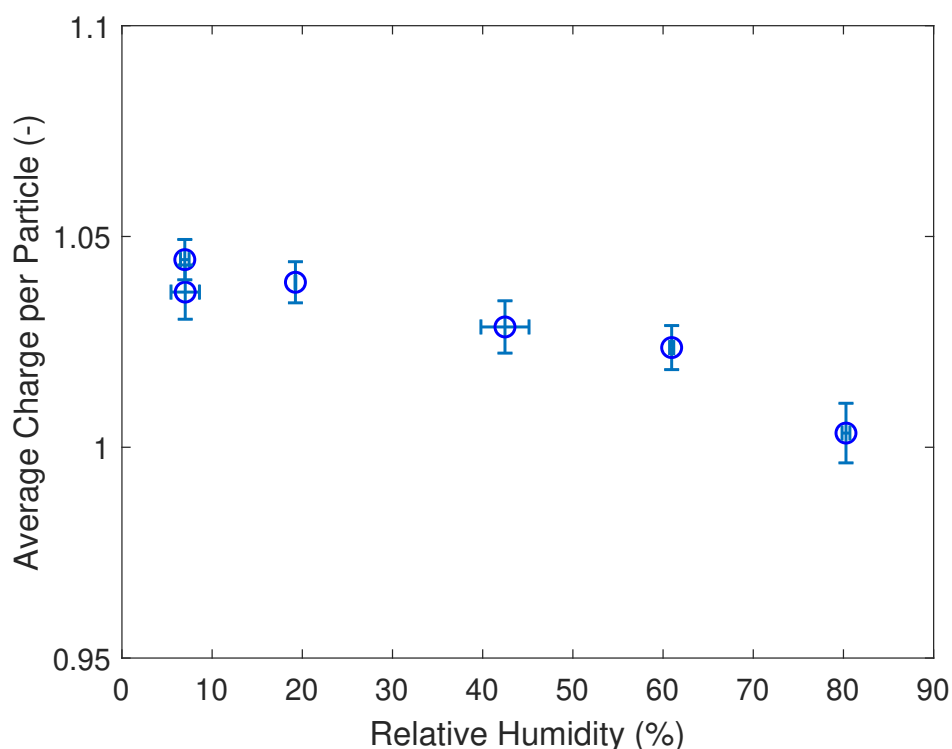


Fig. 3.2 Single charge calibration of the electrometer CPC charge per particle as a function of humidity. Measurements were performed by size selecting a 400 nm mobility diameter aerosol with both the AAC and DMA. Error bars represent one standard deviation in the measurement.

The slight difference in charge calibration is attributed to the sensitivity of the flow meter within the electrometer to humidity. The volumetric flow rate relative to the value measured at dry conditions ( $RH \sim 2\%$ ) as a function of humidity is displayed in Figure 3.3 for nominal electrometer set-points of  $1 \text{ L min}^{-1}$ ,  $1.5 \text{ L min}^{-1}$  and  $4 \text{ L min}^{-1}$ . The volumetric flow rate monotonically decreases with humidity for all flow rates, with a maximum observed difference of - 3.9% at 80% RH. In this work, the electrometer set-point was not varied to account for this and remained fixed for all measurements. Therefore, the measured value of flow through each charger was slightly affected by humidity. However, a 4% change in flow rate, whilst larger than the quoted uncertainty of the flow meter (2%) [203], is not significant enough to alter the trends shown in the resulting analysis. This variation in flow rate has therefore been included as an uncertainty, as discussed in the next section.

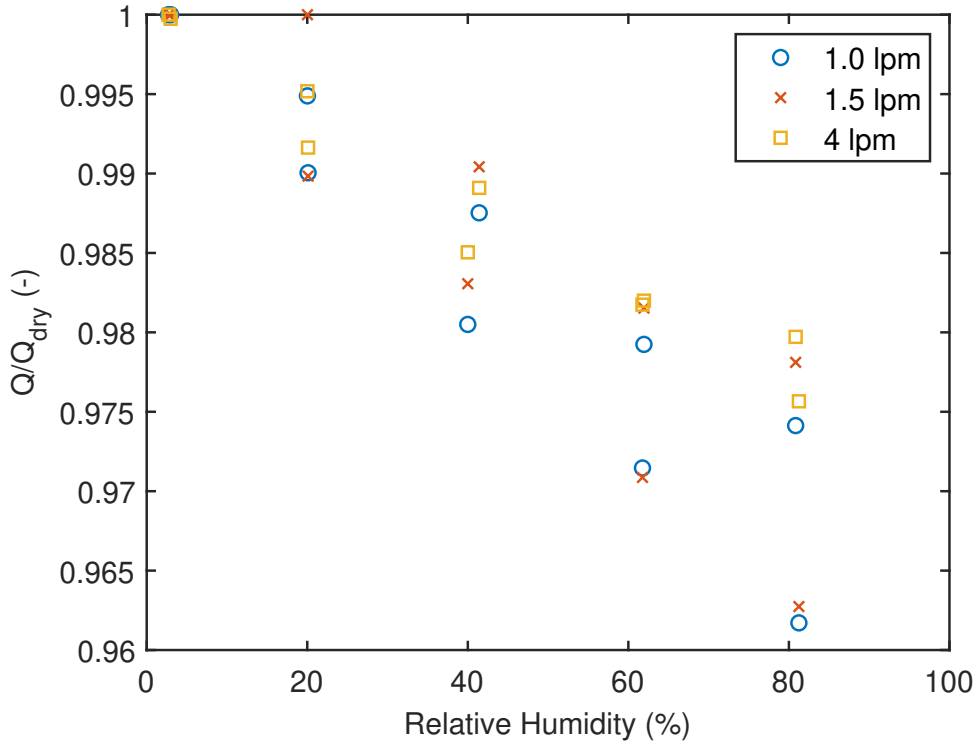


Fig. 3.3 Effect of humidity on electrometer flow rate.

### 3.3.3 Measurement Uncertainty

The charge per particle was calculated using equation 6.14. For all reported measurements of mean charge, error bars represent combined Type A and B uncertainties. Type A uncertainties are taken as one standard deviation (i.e.  $1\sigma$ ) over the measurement period. Type B uncertainties represent the bias uncertainty determined by error propagation of Equation 6.14 according to Abernethy et al. [1]. The bias uncertainty in mean charge,  $u_{\bar{q}}$  is given by

$$\frac{u_{\bar{q}}}{\bar{q}} = \sqrt{\left(\frac{u_{Q_a}}{Q_a}\right)^2 + \left(\frac{u_N}{N}\right)^2 + \left(\frac{u_i}{i}\right)^2} \quad (3.06)$$

where  $u$  represents the uncertainty in the corresponding variable. There is an assumed 5% uncertainty in number concentration as specified by the user manual [204]. The electrometer flow is said to be accurate to within 2%; however, in this work, a 4% uncertainty due to the increased uncertainty of the electrometer flow rate to changes in humidity is assumed. There is 2% or 5 fA uncertainty in the electrometer current (whichever was found to be more significant) [203]. Uncertainty in particle size is taken as 5% for AAC measurements [195] and 3.3% for DMA measurements [96].

### 3.3.4 Ion Mobility Measurements

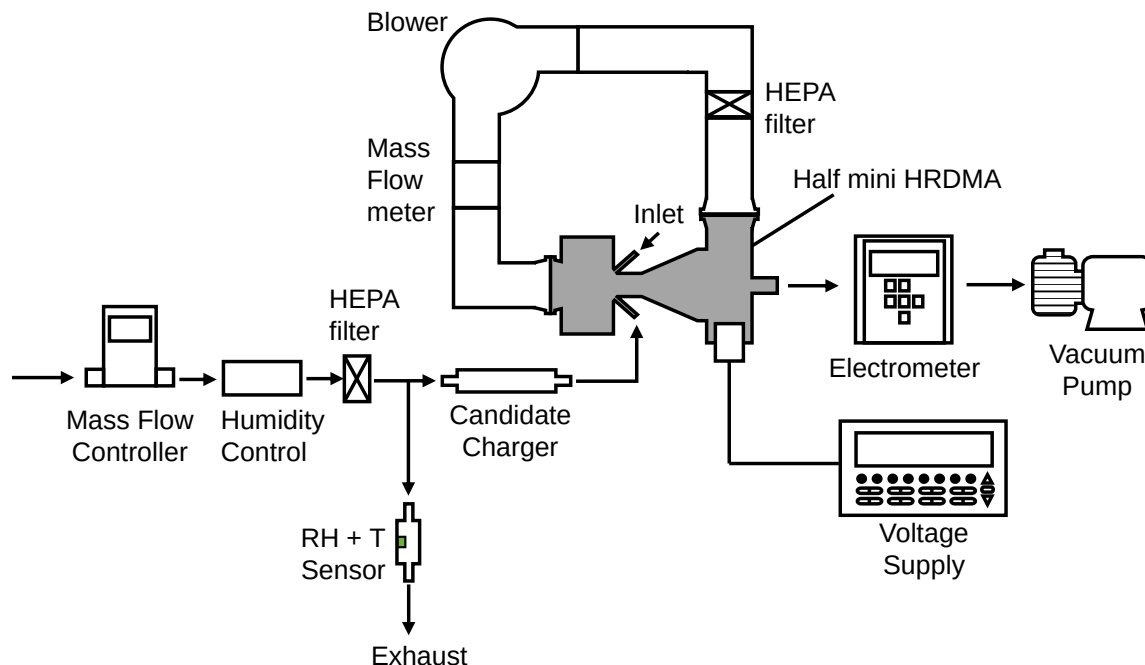


Fig. 3.4 A schematic of the experimental set-up used to measure the ion-mobility spectrum of a candidate charger using a High-Resolution DMA. The half-mini HRDMA is indicated in grey, connected to a recirculating sheath flow loop.

Separate from measurements of mean particle charge, the ion-mobility distributions of the  $^{85}\text{Kr}$  and ELPI charger were measured at five different relative humidity conditions using the experimental set-up depicted in Figure 3.4. Here, the ELPI was operated with an external power supply (Model Bertan 205B - 10R) and operated at a slightly lower voltage 4 kV due to limitations of the power supply. In addition, the ion-mobility distribution of a Soft X-ray (TSI Inc.: Model 3087) was measured. The Soft X-ray charger was not utilised in the mean charge measurements as there were concerns over its neutralisation performance as the unit was purchased in 2011, and older Soft X-ray chargers can exhibit poor charging performance [80, 220]. To measure the ion-mobility distribution as a function of humidity, a HRDMA was employed. An HRDMA can be operated with significantly larger sheath flows than conventional DMAs, minimising diffusing broadening and maximising transmission for sub 3 nm particles [186, 40]. Filtered compressed air was humidity-controlled in the same manner as the mean-charge experiments, and the humidity was measured by venting excess flow through the same RH and temperature sensor. The flow rate through the candidate

charger, which was equal to the sampling aerosol flow rate into the HRDMA, was controlled to  $4 \text{ L min}^{-1}$  by an electrometer. Stainless steel tubing was used to connect the charger outlet to the HRDMA. The HRDMA employed was the ‘half-mini’ HRDMA (the ‘long/fat’ type, with  $r_1 = 4 \text{ mm}$ ,  $r_2 = 7 \text{ mm}$ , and  $L = 20 \text{ mm}$ ), invented and commercialised by de la Mora and Kozlowski [40]. The HRDMA was operated with a recirculating sheath flow (blower Micronel U85HL-024KH-43) with a sheath flow of approximately  $180 \text{ L min}^{-1}$  (as measured by a Sensirion flow meter model SFM3003 Series). The residence time of particles in the classifier was, therefore,  $0.7 \text{ ms}$ . There was a temperature gradient of  $\Delta T \sim 3^\circ\text{C}$  across the inlet and outlet of the HRDMA due to heat generation by the blower. At the highest humidity set-point for the HRDMA measurements  $70\% \text{ RH}$  at  $\sim 23^\circ\text{C}$ , this equates to a maximum difference of  $12\%$  in RH from the inlet to the outlet of the DMA such that the RH within the HRDMA is slightly lower than at the inlet. However, the water vapour concentration will remain constant as the system was closed due to the use of a recirculating sheath flow. Upon humidity changes  $30 \text{ min}$  was waited to allow the sheath flow and sample flow to equilibrate. The reported humidity corresponds to the measured value of the vented excess flow. The voltage of the HRDMA was stepped via a controllable voltage supply (Keithley Electrometer 6517b). The electrometer measured the current at each voltage set-point with an averaging period of  $5 \text{ s}$ . The average measured current was subsequently used to determine the number concentration using Equation 6.14, assuming each ion has a single charge. The results reported herein are the average of a minimum of 3 repeat scans with the HRDMA of both positive and negative ions. Although both the sheath flow rate and voltage were measured, the HRDMA was calibrated prior to experiments to account for discrepancies between the actual and ideal DMA geometry, as well as potential errors in the sheath flow and voltage measurements. The HRDMA was calibrated by electrospraying a solution of methanol and tetra-heptyl ammonium bromide (THAB, 99% Fisher Scientific), the ion of which has a known mobility in dry air [206] of  $0.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The calibration set-up and results are shown in Appendix B.1.

More recent studies using HRDMAs have opted to account for the transfer function of the system used to determine the ‘true’ distribution sampled by the HRDMA system [159, 215, 187]. An effort is also made to account for the DMA transfer function, including entrance and exit losses, as well as diffusive losses of particles within the intermediate tubing between the charger outlet and electrometer inlet. The lognormal electrical mobility distribution can be determined from the raw measurement of number concentration  $N_m(Z^*)$  by,

$$\left. \frac{dN}{d \log Z} \right|_{Z^*} = \frac{N_m(Z^*) \cdot \ln(10)}{\eta|_{d_m^*} P_{\text{Tube}}|_{d_m^*} \lambda_{\text{DMA}}|_{d_m^*} \int \frac{\Omega(V, Z^*)}{Z} dZ}. \quad (3.07)$$

The form of Equation 3.07 is similar to that of a conventional DMA inversion [188]. The transfer function of the HRDMA,  $\Omega(V, Z^*)$  is the diffusing transfer function determined by the method of Stolzenburg [188]. Also included are two additional penetration terms.  $P_{\text{Tube}}|_{d_m^*}$  is the penetration of particles of a given mobility diameter through sampling tubes before and after the HRDMA and  $\lambda_{\text{DMA}}|_{d_m^*}$  is a penetration factor which experimentally approximates losses within the HRDMA due to non-idealities and inlet and exit effects [27]. The counting efficiency of the electrometer,  $\eta|_{d_m^*}$  was assumed to be one for all particle sizes. Both  $P_{\text{Tube}}|_{d_m^*}$  and  $\lambda_{\text{DMA}}|_{d_m^*}$  are evaluated at the equivalent mobility diameter,  $d_m^*$ , of the electrical mobility set-point  $Z^*$  of the DMA. The mathematical forms of  $\Omega(V, Z^*)$ ,  $P_{\text{Tube}}$  and  $\lambda_{\text{DMA}}$  as well as the derivation of Equation 3.07 are given in Appendix B.2. As both penetration terms and the diffusing transfer function of the DMA are functions of particle mobility diameter, a conversion between electrical mobility and mobility diameter is required. The conversion from electrical mobility to particle mobility diameter was performed using the conventional Stokes-Milikan relationship

$$Z_p = \frac{qeC_c(d_m)}{3\pi\mu d_m}. \quad (3.08)$$

where  $q$  is the number of charges on the ion, which is assumed to be one.  $C_c(d_m)$  is the Cunningham slip correction factor, and  $\mu$  is the fluid viscosity, which is assumed to both follow the empirical forms determined by Kim et al. [93]. The conversion between electrical mobility and mobility diameter can be performed in a number of ways. Li and Wang [110] summarised different formulations of the drag coefficient, which consider other important factors such as the radius of a gas molecule and a momentum accommodation factor. As losses are functions of diameter, not electrical mobility, the formulation of the relationship between these two quantities might influence inversion. However, elucidating the impact of different formulations of drag coefficients on data inversion is beyond the scope of this work. Note that the actual diameters indicated within the results are mobility equivalent sizes and, as such, should not be taken as an indicator of the actual geometric size of the ions measured.

## 3.4 Results and Discussion

### 3.4.1 Ion Mobility Measurements

The ion electrical mobility distributions for a TSI 3077 (<sup>85</sup> Kr), TSI 3087 Soft X-ray and ELPI charger operated at  $\pm 4$  kV measured at five different humidities are shown in Figure 3.5. The left and right columns correspond to positive and negative ions, respectively, with each row corresponding to a different aerosol charger, as indicated in the top left-hand corner

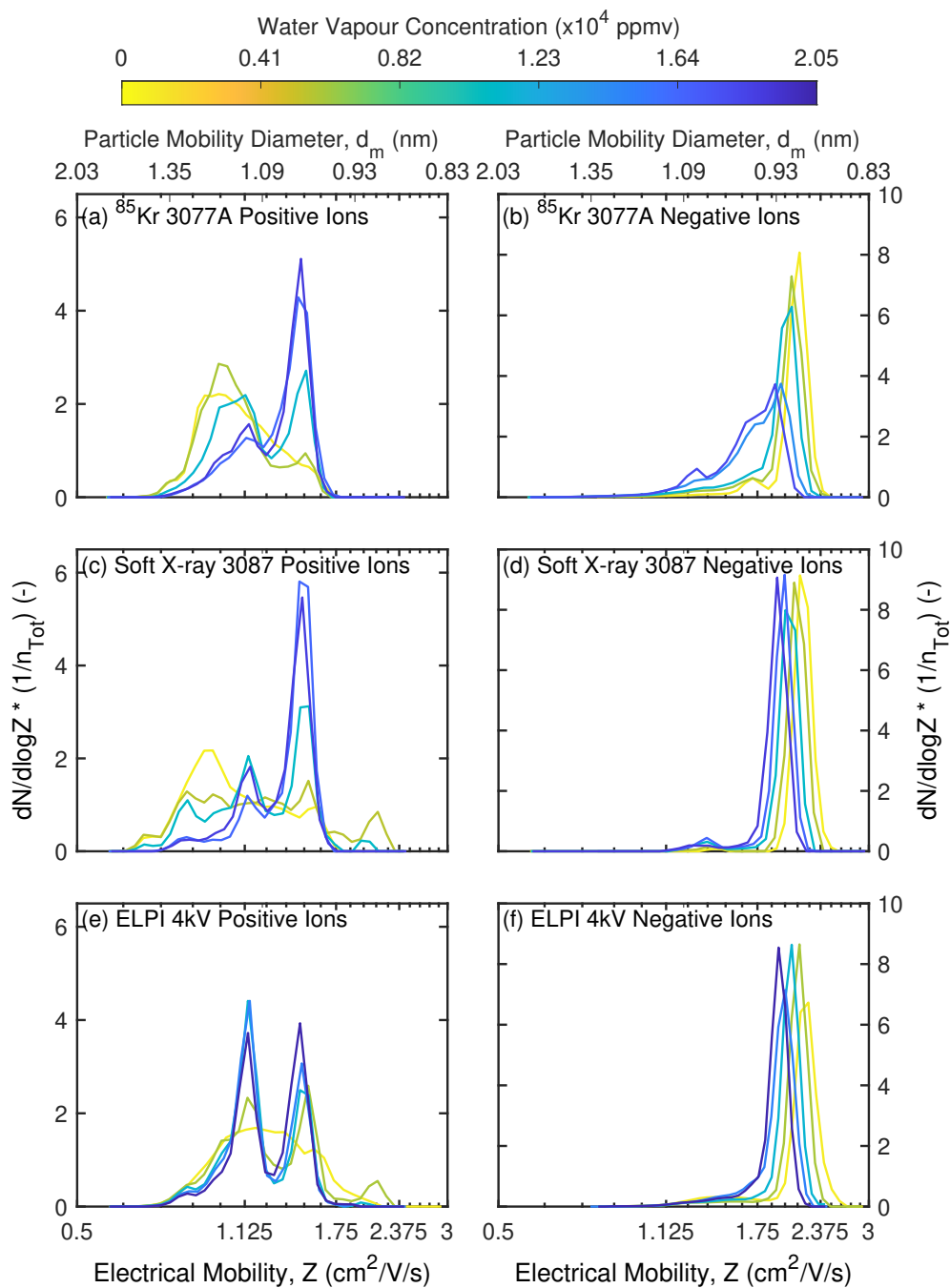


Fig. 3.5 Ion electrical mobility distributions from three different aerosol chargers at five different relative humidity set-points. The left and right columns refer to positive and negative ions from a  $^{85}\text{Kr}$  (Fig. (a) and (b)), Soft X-ray Charger (Fig. (c) and (d)), and an ELPI charger (Fig. (e) and (f)), The legend indicates the water vapour concentration.

of each figure. It is immediately apparent that humidity significantly impacts ion mobility distributions for all chargers, and there are several observable trends in the distributions of both positive and negative ions as humidity increases.

The electrical mobility distributions of negative ions are extremely similar for all three chargers for water vapour concentrations less than  $\sim 11\,000$  ppmv. All three chargers exhibit a dominant peak electrical mobility at approximately  $2.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  with a small shoulder at lower mobilities. The negative ion distribution is extremely monodisperse, which has also been found by other authors Alonso et al. [7]. The similarity in negative electrical mobility distribution between a corona charger and radioactive charger ( $^{241}\text{Am}$ ) was also found by Alonso et al. [7]. The peak electrical mobility at dry conditions for both chargers evaluated in their work were approximately  $2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  similar to values found here. However, the similarity between the ions produced by different charging mechanisms found in this work directly contradicts Kallinger et al. [87], who found that four different bipolar chargers, including those using radioactive sources, had similar positive ion spectra but dissimilar negative ion spectra. Without confirmation of the species of ions present, it is hard to discern the difference between our results and those of Kallinger et al. [87]. Despite its common use over the last 20 years within SMPS systems, there are very few ion mobility measurements of the TSI 3077A charger. Leppä et al. [106] measured the average negative mobility using Radial Opposed Migration Ion and Aerosol Classifier to be  $1.53\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  in filtered laboratory air, the humidity during this work is not specified. This value is significantly lower than the present measurements. The measurement of other radioactive charging sources using HRDMAs place their average negative electrical mobility closer to  $2.05\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , which is similar to this work [187, 7, 87].

As humidity increases, the negative ion mobility distributions shift to lower mobilities (or larger equivalent mobility diameters). The soft X-ray and ELPI peaks shift similarly, with the widths of the peaks remaining relatively constant as humidity increases. However, the distribution of negative ions from the  $^{85}\text{Kr}$  charger not only shifts to lower electrical mobilities but also starts to broaden with multiple peaks present at conditions of higher humidity conditions. The mobility shift observed in all three chargers is likely due to the clustering of ions with water molecules. Liu et al. [114] measured both the mobility distribution and mass spectra of ions produced by a TSI 3087 Soft X-ray Charger, the same Soft X-ray Charger used in this study, by combining DMA measurements with a Mass Spectrometer. In dry (6% RH) filtered laboratory air conditions, they found peak negative electrical mobilities of  $2.25\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  which decreased to  $1.89\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at 61% RH which is very similar to values of  $2.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  and  $1.9\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at similar humidity levels in this work. With the addition of a chemical composition measurement, they found

that negative acid radical ions tend to cluster with water molecules. Earlier ion measurements by [103] in nitrogen found the peak electrical mobility increased from  $1.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  to  $1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  as the carrier gas was dried which is contradictory to our findings and the findings of Liu et al. [114]. Measurements by the same author of a radioactive  $^{241}\text{Am}$  charger provided similar results in which the negative ions were found to increase in mobility as a function of humidity, again in disagreement with our measurements from a Krypton source. Manninen et al. [121] also found that the negative ions in a unipolar charger decreased in mobility as the humidity was increased, similarly suggesting the mechanism being the accumulation of water molecules on ion clusters.

Positive ions exhibit a much more polydisperse distribution than their negative counterparts. For dry conditions, the positive ion distribution is extremely broad with a peak intensity close to  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for all three chargers. As humidity increases, all three chargers exhibit a peak at  $\sim 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . At  $\sim 6000 \text{ ppmv}$  both the ELPI and Soft X-ray chargers show ions located at an electrical mobility of  $2.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  which are not present at any other RH conditions, potentially suggesting the production of new ion species at lower water vapour concentration, which subsequently cluster and grow to larger sizes. A peak can also be seen at lower electrical mobilities, and the intensity and location of this peak varies from charger to charger as a function of humidity. For both the bipolar chargers, the left-hand portion of the distribution shifts to higher electrical mobilities as humidity increases and intensity decreases. Whereas for the ELPI, the second peak is fairly monodisperse and increases with intensity up to  $\sim 6000 \text{ ppmv}$ , after which the number of ions present at this mobility is approximately constant. Above  $\sim 6000 \text{ ppmv}$ , this peak is consistently located for all chargers at  $\sim 1.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

In contrast to negative ions, which are hypothesised to cluster with water molecules, resulting in a shift towards lower electrical mobilities, positive ions demonstrate a distributional change indicative of increased electrical mobility in the presence of water molecules compared to dry conditions. This contrasts with the findings of Liu et al. [114], who observed minimal influence of relative humidity on the dominant peak electrical mobility, which remained consistent at  $0.93 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  under laboratory air conditions using the same model of Soft X-ray charger, regardless of RH levels at 6% and 61%. However, they noted the emergence of a new secondary peak exhibiting higher electrical mobility at  $1.63 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at the higher humidity condition. Additionally, measurements conducted by the same author in a separate study identified an additional peak of increased mobility in the positive ion spectra when analysing ambient air [113]. The findings of Liu et al. [114] are supported by Lee et al. [103], who found humidity had a minimal effect on positive ions produced by a soft X-ray charger. However, the results shown here diverge from these findings, as significant

alterations in both the location and intensity of the distribution of positive ions with varying humidity levels are observed, seemingly resulting in the presence of a greater proportion of more mobile positive ions. However, it should be noted Lee et al. [103] conducted their measurements with a TSI nano DMA model 3085 as HRDMAs did not exist at the time. This model of nano DMA is unsuitable in accurately measuring particles smaller than 2 nm owing to increased diffusional effects. The discrepancies observed may be attributed to differences in contaminants and trace gases present within the tubing, as well as variations in carrier gases used, which are likely to vary between laboratories and significantly influence the measured ion spectra [187, 118, 32]. As an example, a silicon diffusion dryer was used in this study to dry the compressed air, which could add different impurities to the system.

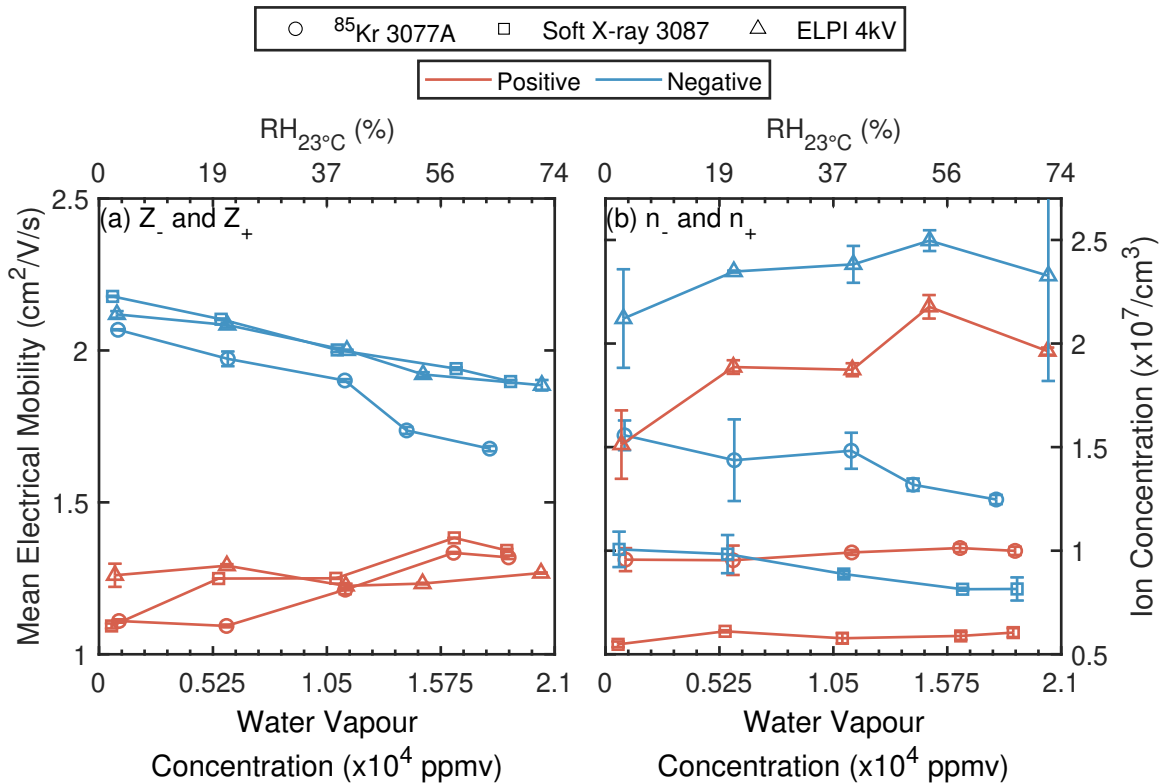


Fig. 3.6 Average ion properties determined from the distributions in Figure 3.5. Figure (a) shows the number-weighted averaged electrical mobility. Figure (b) shows the integrated number concentration for each charger. Red and blue lines correspond to parameters for positive and negative ions of each respective charger (which are indicated by symbols). Error bars represent the repeatability of at least 3 repeat measurements, assuming a t-distribution and 95% confidence interval.

Figure 3.6 summarises the average electrical mobility as well as the total integrated number concentration for each charger as a function of humidity. All average ion measurements are well within the reported literature values of ion measurements, with negative ions more

mobile than positive ions [197]. In general, the humidity decreases the average electrical mobility of negative ions for all charging methods. For both bipolar chargers, the average positive mobility increases, whereas for the corona charger, the average mobility remains relatively constant as a function of equivalent relative humidity. The concentration of ions present in both bipolar chargers was found to be between  $6 \times 10^6 - 1.6 \times 10^7 \text{ cm}^{-3}$ . This is a similar order of magnitude of ion concentration measurements obtained from an HRDMA [187] and other methods [41]. This, therefore, somewhat validates the inversion method used to determine the distribution from the raw measurement signal using Equation 3.07; however, there is still a large amount of uncertainty in the total concentration. It is expected the positive and negative ion concentrations to be equal [197, 41] and that the total concentration of ions is conserved as humidity changes. However, it was found that the concentration of positive and negative ions in each charger is within a factor of 1.5. This discrepancy is likely due to inaccuracies in the loss functions within the inversion.

### 3.4.2 Bipolar Charging Mean Charge Measurements

Figure 3.7 shows the effect of humidity on the average charge attained by a radioactive  $^{85}\text{Kr}$  bipolar charger. Humidity seemingly affects the measured charge, and as the humidity increases, the mean charge increases (*i.e.* becoming more positive). Fitting Equation 3.01 to the experimental data enables a calculation of the ion mobility ratio. Values of the calculated ion mobility ratio as a function of relative humidity are shown in Table 3.1. As humidity increases, the ion mobility increases, trending closer to 1. This suggests that the positive and negative ion mobility values are getting closer together in value as humidity increases. This is in qualitative agreement with the ion mobility measurements, however a more in depth comparison between the ion measurements and the mean charge measurements is provided in the following section. The addition of water vapour can lead to an increase of up to 38% in the mean charge, corresponding to an increase in the ion mobility ratio from 0.843 to 0.898, as shown in Table 3.1. Some hysteresis is observed when the measurement returns to dry conditions after the measurements at higher humidity values. The mean charge is higher by approximately 13% at dry conditions ( $\text{RH} \sim 5\%$ ) when taken at the end of the measurement cycle (light blue triangles in Figure 3.7) compared to the start of the measurement cycle (dark blue circles in Figure 3.7). This may suggest that the ions in the charger may depend on previous humidity values. This warrants further investigation in future work.

The observed trend of bias towards a more positively charged aerosol with increasing humidity aligns with the findings of Liu et al. [113]. Within their work, it was found that between 62% and 89% RH, two SMPS systems using a Soft X-ray and  $^{85}\text{Kr}$  respectively measured up to 60% higher concentrations than a reference CPC when sampling from an

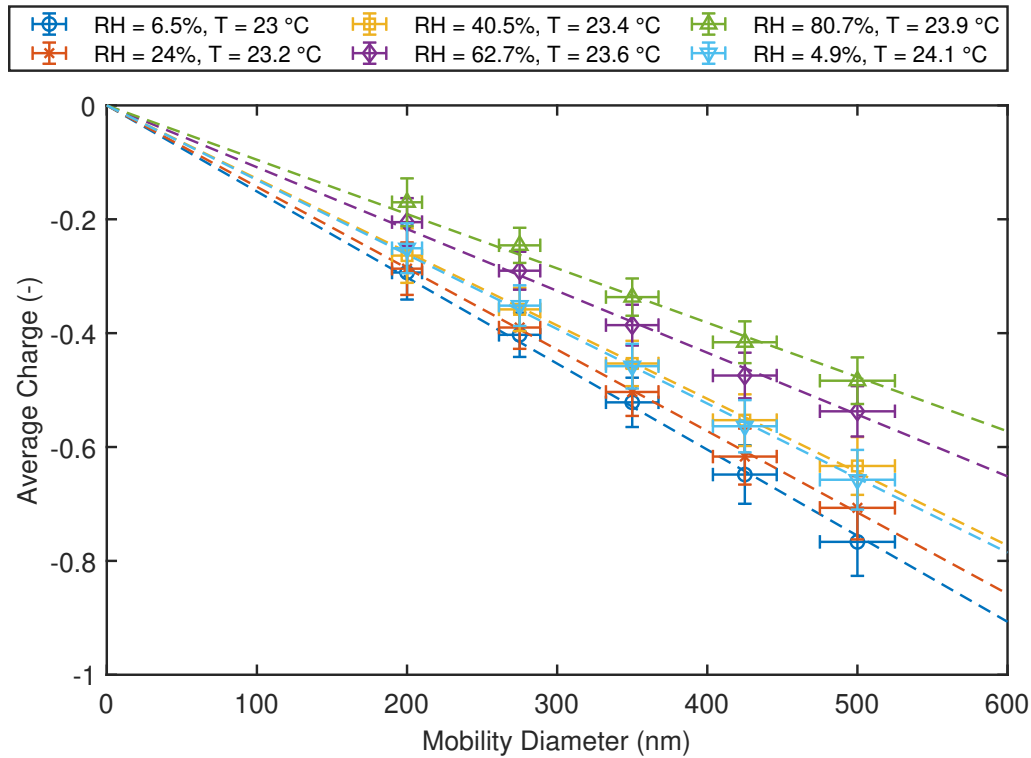


Fig. 3.7 Effect of humidity on  $^{85}\text{Kr}$  bipolar diffusion charger response. Dashed lines are lines of best fit according to Equation 3.01 with fit values given in Table 3.1. Note that data corresponding to an  $\text{RH} = 4.9\%$ ,  $T = 24.1\text{ }^{\circ}\text{C}$  (light blue scatter points) is indicative of hysteresis occurring as this was taken after humidification.

ambient environment. As the DMAs used in their SMPS systems sized positively charged particles (i.e. negative rod voltage), an overestimation in number concentration would occur if the assumed +1 charge fraction used in data inversion underestimated the true +1 charge fraction for particles of a given size<sup>2</sup>. Therefore, this discrepancy in their work suggests a bias towards positive charging in humid environments, which qualitatively corresponds with the findings of this work.

### 3.4.3 Comparison of Bipolar Mean Charge measurements and Ion Mobility Measurements

Figure 3.8a compares the mean charge directly measured (Figure 3.7) to that calculated evaluating Equation 3.01 with the mean ion mobility values of Figure 3.6. Both the experi-

<sup>2</sup>Neglecting the effect of multiply charged particles which would further increase inaccuracies in data inversion [106]

Table 3.1 Parameters for bipolar chargers at different relative humidity obtained through Least Squares Fitting to Equation 3.01. Uncertainty in the fit ion mobility ratio is indicated by a 95% Confidence Interval in brackets. Note that data corresponding to an RH = 4.9%, T = 24.1 °C (light blue scatter points) is indicative of hysteresis occurring as this was taken after humidification.

| T (°C) | RH (%) | $\frac{Z_+}{Z_-}$ (Eq. 3.01) | R <sup>2</sup> |
|--------|--------|------------------------------|----------------|
| 23.0   | 6.5    | 0.843 ( $\pm$ 0.023)         | 1.0            |
| 23.2   | 24     | 0.851 ( $\pm$ 0.014)         | 1.0            |
| 23.4   | 40.5   | 0.865 ( $\pm$ 0.004)         | 1.0            |
| 23.6   | 62.7   | 0.885 ( $\pm$ 0.025)         | 0.99           |
| 23.9   | 80.7   | 0.898 ( $\pm$ 0.04)          | 0.99           |
| 24.1   | 4.9    | 0.863 ( $\pm$ 0.003)         | 1.0            |

mental measurements of mean charge and the ion-mobility calculated mean charge show an increase in the particle charge as a function of humidity (i.e. average charge becomes less negative). However, there is a significant disparity in the absolute magnitude of the mean charge measured experimentally compared to those calculated from the ion mobility values. Using the averaged measured ion values in Equation 3.01 predicts highly asymmetric charging, which is significantly biased towards the negative, which is not observed experimentally. The experimental measurements of mean charge are in line with the ion mobility ratio of 0.875 suggested by Gunn and Woessner [61], as shown in Table 3.1, which is utilised in the SMPS software for the <sup>85</sup>Kr charger rather than values of 0.54 to 0.79 which were measured with the HRDMA.

To highlight both the mean charge measurements and ion mobility measurements exhibit similar trends, the mean charge response normalised to the corresponding value at dry conditions for each measurement/calculation method is shown in Figure 3.8b. This more readily highlights that the absolute net charge on the aerosol decreases relative to the dry value as humidity increases, leading to a maximum difference of about 30 - 40% for the experimental measurement of mean charge. Significantly, the data for each particle diameter converge, highlighting that this phenomenon is relatively consistent across diameters and solely depends on the ion mobility ratio. The normalised mean charge predicted by substituting the measured average ion mobility values into Equation 3.01 also decreases as a function of humidity, although it predicts up to 60% reduction in the absolute mean charge relative to dry conditions. Once normalised, the trends exhibited by both measurements of mean charge and those predicted by substituting the measured average ion mobility values into

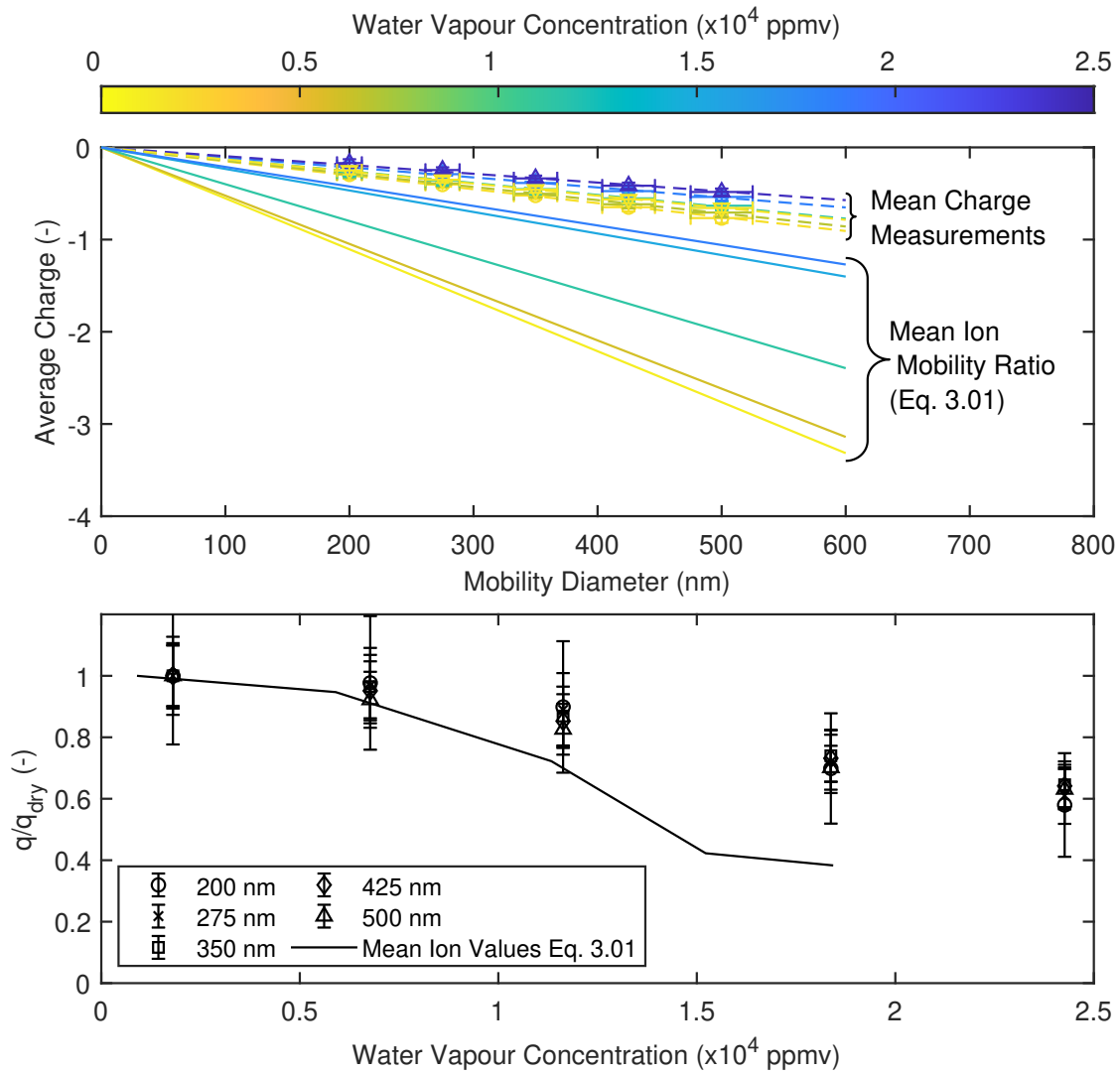


Fig. 3.8 Figure (a) shows the comparison of measured mean charge and the mean charge calculated by substituting the average ion properties in Figure 3.6 into Equation 3.01. The colours of each line/symbol in Figure (a) correspond to the colour bar at the top, indicating water vapour concentration. Solid lines show the mean charge calculated using the mean ion mobility values, whereas symbols and dashed lines show direct measurements of the mean charge. Figure (b) shows the normalised mean charge relative to dry conditions for measured mean charge data (scatter symbols) and ion mobility measurements (solid black line).

Equation 3.01 are in reasonable agreement. As the normalised trend for both the measured mean charge and predicted mean charge from ion mobility measurements using Equation 3.01 are in good agreement with one another, this suggests that the magnitude of the ion

mobility ratio,  $Z_+/Z_-$  measured using the HRDMA is incorrect but the relative change in ratio as humidity is increased is well captured.

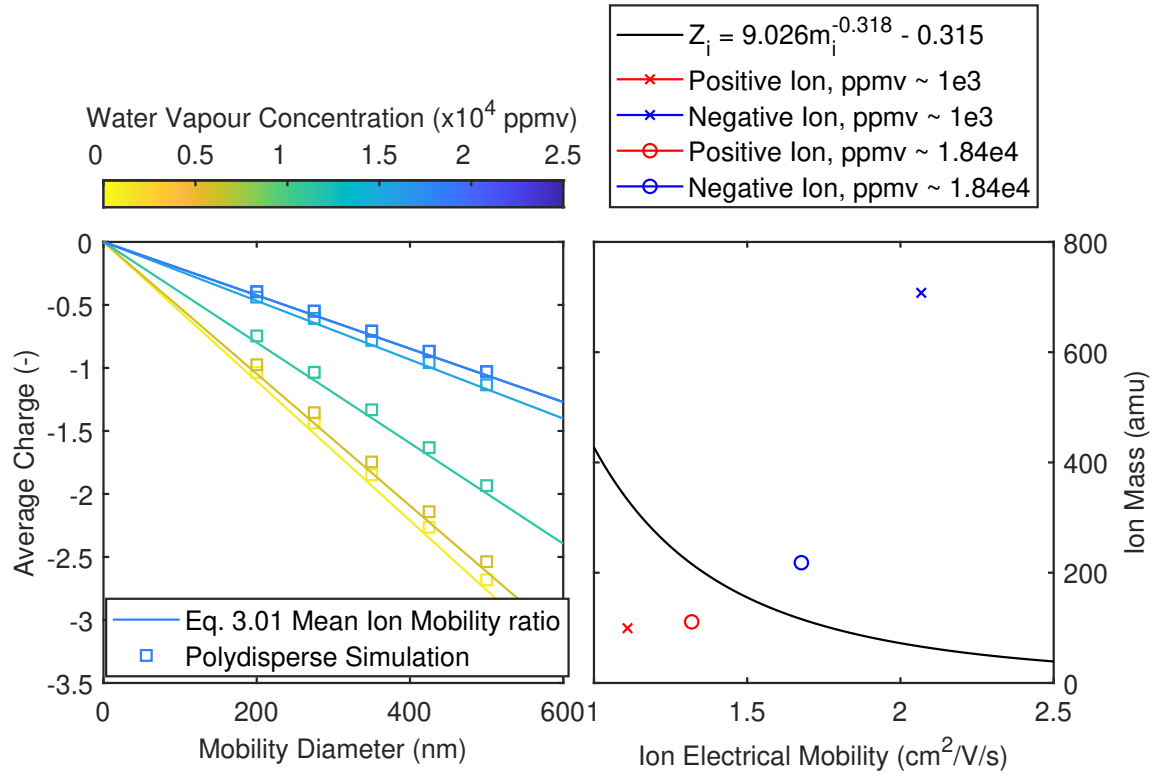


Fig. 3.9 Figure (a) shows a comparison between the mean charge calculated using the average ion mobility ratio and that obtained using the full polydisperse ion distribution in a numerical model. Figure (b) compares an empirical mass-mobility relation (solid black line) from Steiner et al. [186] and the average mass and mobility of positive and negative ions required to match the experimentally measured mean charge data to the ion mobility measurements. This matching was performed at two different humidity concentration values.

The discrepancy between the mean charge measurements and ion mobility measurements were investigated further with a numerical model. It was thought that potentially using an average ion ratio may result in errors in the calculation of mean charge. Numerical simulations were performed based on the work of Fuchs [49] with modifications from Hoppel and Frick [71]; the model is described in Appendix A.2. These simulations utilize the full polydisperse ion mobility distributions illustrated in Figure 3.5 rather than relying solely on the average ion mobility to compute the mean particle charge using Equation 3.01. As shown in Figure 3.9a, using average values makes little difference to the calculated mean charge, agreeing with the work of Carsí and Alonso [28]. Therefore, another cause of disparity between ion mobility and mean charge measurements must exist. Another possible

cause may be differences in ion masses than typically determined by empirical correlations to relate ion mobility to ion mass [186, 119]. The ion's mass is used to calculate the ions' mean thermal velocity and the ion diffusion coefficient, which are used to calculate the ion-aerosol attachment coefficient. Matching the experimental measurement of mean charge to the ion data using the ion masses as two free parameters within the numerical model indicates how far the mass would have to vary from typically assumed values. Figure 3.9b demonstrates that the mass required to match the ion measurements to charge measurements represents significant deviations relative to the empirical model. To obtain similar charge values, the mass of negative ions has to increase. In contrast, the positive ion mass has to decrease, which suggests an increase in ion mass as mobility increases. This is in significant contradiction to measurements of ion mass in the literature. As such, it is unlikely to be the cause of the discrepancy [186, 114, 119]. The only other variable which can be considered is the ion concentration in the charging volume. Note in Gunns' original work, the ionic ratio in Equation 3.01 is given as  $n_+Z_+/n_-Z_-$  and it is assumed that the ion concentrations are equal such that they cancel. To match ion measurements to mean charge measurements, there would have to be more positive than negative ions in the charging volume. However, literature shows that the ion concentrations are approximately equal within bipolar chargers [41, 102].

Whilst the large discrepancy between the mean charge predicted using ion mobility values and the measured mean charge found in this work is somewhat alarming, there are several other instances of disagreement between direct charge measurements and ion mobility measurements within the literature. Reischl et al. [163] found their measured mean ion mobility values from a  $^{241}\text{Am}$  source of  $1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for negative and positive ions respectively did not fit their experimental charge measurements. To obtain a better match between theory and experiment, they reduced the negative ion mobility to  $1.425 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , thereby increasing the ion mobility ratio from 0.61 to 0.77. An ion ratio value of 0.61 for their radioactive charger is similar to the value of 0.54 measured for the  $^{85}\text{Kr}$  radioactive charger at low water vapour concentrations in this work. Tauber et al. [193] characterised a new plasma charger and compared its charging efficiency to a commercial TSI X-Ray (TSI Inc, Model 3088) and a radioactive  $^{241}\text{Am}$  bipolar diffusion charger for particles between 4 nm to 12 nm. Comparisons between the theoretical charge distribution determined using average quantities of measured ion mass-mobility spectra and the measured charge distribution showed poor agreement, with the theoretical charge distribution over-predicting the negative charge fraction. By correcting the charge distribution, utilising ion values summarised by Reischl et al. [163], the measured charge distribution showed better agreement with theory. It should be noted, however, that their work investigated small particles in which charging theory is often not representative relative to experiments [73, 41].

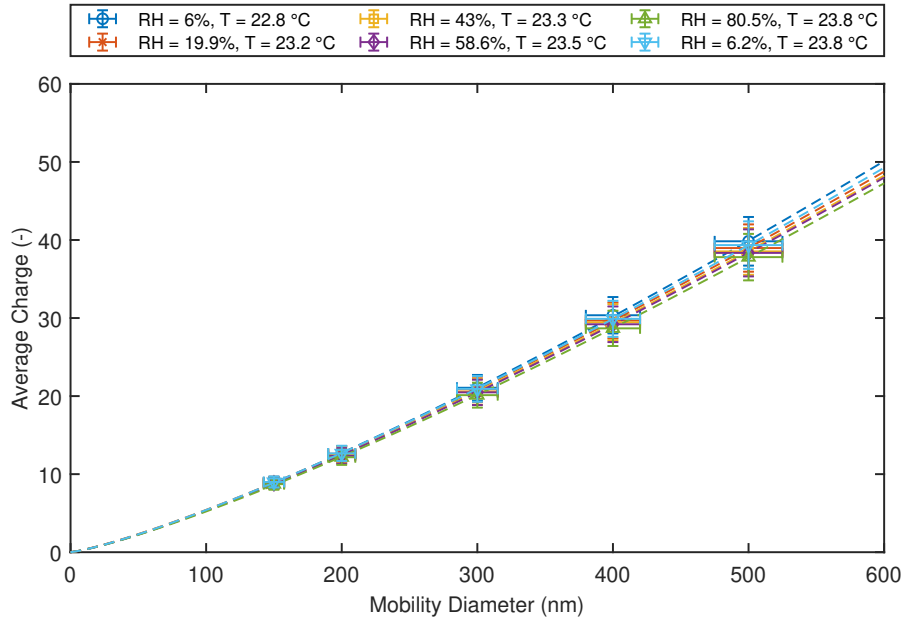


Fig. 3.10 Effect of humidity on ELPI unipolar charger response. Dashed lines are lines of best fit according to Equation 3.03 with fit values given in Table 3.2

More recently, Liu et al. [113] used a soft X-ray and  $^{85}\text{Kr}$  SMPS in a varying ambient humidity environment to measure particle size distributions. The mean ion mobility ratio, used to determine charge fractions within the TSI AIM software, was set to be 0.975 and 0.875 for the Soft X-ray and Kr neutralisers, respectively. This enabled extremely good agreement between SMPS distributions measured by the two chargers. However, they also measured the ion mobility distributions generated by the soft X-ray charger in air (19% RH). They found an ion mobility ratio of 0.558, similar to values found within this work utilising the same model of Soft X-ray charger. This ion mobility ratio would result in highly asymmetric charging, leading to SMPS inversion errors. As no significant errors were reported between measurements with the two SMPS systems, this would suggest that the ion mobility values used within the inversion are accurate, thus highlighting another instance of discrepancies between ion mobility measurements and charging measurements. The cause of the discrepancy between ion and charge measurements requires further work to elucidate.

### 3.4.4 Unipolar Diffusion Charging: Mean Charge Measurements

Figure 3.10 shows the effect of humidity on the mean charge for the ELPI unipolar charger. There is a slight decrease in charge as humidity increases, but it is less than 8% and within the measurement uncertainty. This means that only slight variations in calibration values

are obtained by regression fitting to Equation 3.03, and fit values for both the constant and exponent lie within the confidence interval of the regression analysis. This response is different relative to the effects on bipolar charger and can be explained by the current-controlled operation of the ELPI. Maintaining a constant charging current is a proxy for maintaining a constant ion concentration within the charging volume. Therefore, the  $n_i t$  remains approximately constant regardless of how conditions change. Thus, mass and mobility are the only other ion parameters that can vary. These results are similar to those of Schriebl et al. [173], who found that the counting efficiency of a pulsed mode diffusion charger utilising a wire-based charging module did not vary significantly from dry conditions (2% RH) to humid conditions (62% RH). The results herein cannot directly be compared to the work of Yawootti et al. [225] as they utilised a constant voltage (rather than constant current) charger. Constant voltage operation of the ELPI was attempted to examine the effect of humidity as the voltage was varied. Similar trends of greater sensitivity of charging to humidity at lower applied electrode voltages demonstrated in the work Yawootti et al. [225] were found. However, the stability of the charger was found to be extremely poor at lower voltages ( $\leq 3$  kV). These results are therefore not included in the results of this study.

Whilst the full mass-mobility spectra of the ions in the charger are not available, some assumptions can be made to evaluate the role of ion properties in unipolar charging. Firstly, it should be noted that although the ion mobility measurements were taken at a lower voltage than the mean charge measurements (4 kV compared to 5 kV). However, it can be assumed that the mean ion mobility takes a value between  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  regardless of the applied electrode voltage and humidity as shown by other studies [7, 121]. Based on the measurements of mean charge, an approximate  $n_i t$  product can be determined by matching Lawless' Charging theory, which includes terms for both field and diffusion charging [101], to the experimental data. For an electric field strength in the charger of  $1.67 \times 10^5 \text{ V m}^{-1}$  [150] and assuming an ion mobility value of  $1.15 \text{ cm}^2 \text{ V}^{-1} \text{ m}^{-1}$ , as per the average given by the ion mobility measurements, yields an  $n_i t$  value of  $2.3 \times 10^{13} \text{ s m}^{-3}$ . Variations in ion mobility between  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at this  $n_i t$  value lead to maximum absolute variations in charge of 10.6%, relative to an ion value of  $1.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Therefore, ion property changes are seemingly less important in the performance of a unipolar charger.

### 3.4.5 Photoelectric Charging

Figure 3.11 demonstrates the response of the photocharger as a function of humidity, indicating a decrease in the particle charge as the humidity increases. The mean charge decreases by up to 27% from  $\sim 5\%$  to 80% RH. A small amount of hysteresis ( $\sim 5.5\%$ ) was observed when going back down from 80% to 4% RH. This reduction in mean charge results in a

Table 3.2 Parameters for ELPI unipolar charger at different relative humidity obtained by least squares fitting to Equation 3.03 . Uncertainty each fitting parameter is indicated by a 95% Confidence Interval in brackets.

| T (°C) | RH (%) | $q_0$ (Eq. 3.03)       | $\nu$ (Eq. 3.03)    | $R^2$ |
|--------|--------|------------------------|---------------------|-------|
| 22.8   | 6.0    | 0.0171( $\pm$ 0.0026)  | 1.25 ( $\pm$ 0.025) | 1.0   |
| 23.2   | 19.9   | 0.0192 ( $\pm$ 0.0012) | 1.23 ( $\pm$ 0.011) | 1.0   |
| 23.3   | 43.0   | 0.0190( $\pm$ 0.0017)  | 1.23 ( $\pm$ 0.015) | 1.0   |
| 23.5   | 58.6   | 0.0185( $\pm$ 0.0017)  | 1.23 ( $\pm$ 0.016) | 1.0   |
| 23.8   | 80.6   | 0.0181 ( $\pm$ 0.0020) | 1.23 ( $\pm$ 0.018) | 1.0   |
| 23.8   | 6.2    | 0.0185( $\pm$ 0.0013)  | 1.23 ( $\pm$ 0.012) | 1.0   |

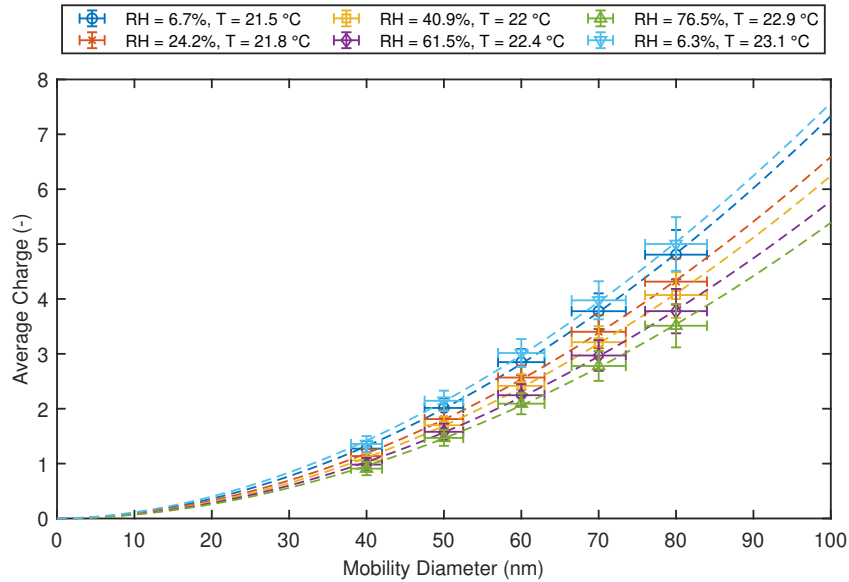


Fig. 3.11 Effect of humidity on photocharger response for silver particles. Dashed lines are lines of best fit according to Equation 3.04 with values given in Table 3.3

decrease in the proportionality constant,  $c$ , in Equation 3.04 whilst the exponent,  $x$ , remains approximately constant (see Table 3.3). The exponent is close to 2 indicating that the mean charge approximately scales with particle surface area corroborating previous studies [136].

The mechanism for the reduction in the mean charge is likely different from previous discussions for diffusion chargers. Unlike unipolar and bipolar charging, any change in ion properties will likely be inconsequential as ion-particle recombination is limited owing to the applied electric field within the charging chamber [135]. Changes in ion properties can, therefore, be considered a second-order effect. There are three main hypotheses about

Table 3.3 Power law regression fitting parameters for photocharger measurements at different relative humidity. Uncertainty in the regression fit parameters is indicated by a 95% Confidence Interval in brackets.

| T (°C) | RH (%) | c (Eq. 3.04)                                   | x (Eq. 3.04)       | $R^2$ |
|--------|--------|------------------------------------------------|--------------------|-------|
| 21.5   | 6.73   | $0.0013(\pm 5.1 \times 10^{-4})$               | $1.87 (\pm 0.091)$ | 1.0   |
| 21.8   | 24.2   | $0.0012 (\pm 5.7 \times 10^{-4})$              | $1.87 (\pm 0.11)$  | 1.0   |
| 22     | 40.9   | $0.0011(\pm 5.6 \times 10^{-4})$               | $1.89 (\pm 0.13)$  | 1.0   |
| 22.3   | 61.5   | $9.96 \times 10^{-4}(\pm 5.2 \times 10^{-4})$  | $1.88 (\pm 0.12)$  | 1.0   |
| 22.9   | 76.5   | $9.21 \times 10^{-4} (\pm 5.6 \times 10^{-4})$ | $1.88 (\pm 0.14)$  | 1.0   |
| 23.0   | 6.2    | $0.0017(\pm 8.3 \times 10^{-4})$               | $1.83 (\pm 0.12)$  | 1.0   |

how humidity might influence the photocharging process. The first potential dependence on humidity is the production of water droplets by UV light in the presence of water vapour [227]. The total concentration and current attributed to generated water droplets at an RH of 80% were measured downstream of the photocharger with a HEPA filter on the front of the device, which means any particles measured by the CPC must have been produced in the photocharger. It was found that a steadily increasing number of particles were generated in the device as humidity was increased. A particle concentration of  $10 \text{ cm}^{-3}$  were present at 4% RH which increased to  $3.7 \times 10^4 \text{ cm}^{-3}$  at 80% RH. However, these particles contributed negligibly to the electrometer current ( $\pm 0.3 \text{ fA}$ ). Therefore, the production of water droplets was deemed not to impact the current measurement. However, it may indirectly affect particle charging as photons are used to create particles rather than charge the aerosol, which may act to reduce the particle charge as shown in Figure 3.11. The other two hypotheses are that water adsorbed to the particle surface changes the state of the surface, which can influence the photoemission process and/or UV light is attenuated by water vapour present in the charging volume such that the charging decreases as a function of humidity. Silver particles are hydrophobic and, as such, do not uptake water very easily; for the humidity values investigated in this work, there will be no growth of particles to larger sizes. As such, any effect of water adsorption/ particle growth can be disregarded. It is, therefore, likely that the attenuation of the UV light within the charging volume is the cause of the reduction in mean charge. The obtained results corroborate this. Referring back to Equation 3.04, the observed reduction in the proportionality constant with humidity (Table 3.3) indicates a reduction in the irradiation intensity as the flowrate, quantum yield, and photoelectrically active surface area can be considered approximately constant parameters.

## 3.5 Conclusions

Within this work, the effect of humidity on three commonly used particle charging techniques has been evaluated through the measurement of mean particle charge and ion mobility spectra. Measurements of inverted ion mobility spectra obtained using a High-Resolution DMA demonstrate a significant effect of humidity on ions produced by two different bipolar chargers and a unipolar charger. Negative ion spectra remain approximately mono-mobile as humidity increases, but they shift towards lower electrical mobilities, potentially due to ion-ion clustering. Positive ion spectra are much broader than their negative counterparts, but as humidity is increased, the positive spectra narrow. Furthermore, unlike the negative ions, it was found that the addition of water vapour resulted in positive ions that became more mobile.

Measurements of the average charge on a monodisperse aerosol reveal that humidity influences various charging mechanisms uniquely. For radioactive bipolar chargers, the mean charge on a monodisperse aerosol increased (i.e. became more positive) by up to 38%, indicating the ion mobility ratio was increasing. Comparison of measured mean charge relative to that predicted using the measured ion spectra exhibited consistent trends but varying magnitudes in the expected charge. A unipolar corona charger operating in a current-controlled manner was found to be relatively insensitive to changes in humidity. Mean charge measurements of a direct UV photoelectric charger showed that as humidity increases, the charge per particle decreases by up to 30%, which was attributed to the attenuation of UV light within the charging chamber.

This study highlights the importance of recognising potential measurement artefacts that may arise when using charging-based sensors in environments with varying humidity. The findings are particularly relevant to aerosol scientists and instrumentation developers who rely on particle charging techniques for aerosol characterisation, especially in environmental or industrial applications where humidity levels can fluctuate significantly. This is especially pertinent for users of bipolar chargers, both in the contexts explored here and in more routine Scanning Mobility Particle Sizer (SMPS) measurements, where it is typically assumed that the aerosol reaches a steady-state charge distribution. Variations in relative humidity may compromise this assumption, thereby influencing data inversion procedures and potentially leading to inaccurate conclusions.



## Chapter 4

# Multiple Charge Correction in Particle Mass Analysers: Experimental Validation of the Interpolated Average Charge (INTAC) Algorithm <sup>1</sup>

### 4.1 Introduction

Aerosol classifiers are often used to produce an approximately monodisperse aerosol by selecting a narrow range of particles of a given property from an underlying polydisperse distribution. The generation of a monodisperse aerosol is useful for evaluating other instrumentation such as particle counters [168, 201, 64], investigating particle morphology [195, 128, 181, 89, 202] and hygroscopic growth [17, 68] or evaluating aerosol chargers [141, 81, 78, 223], to name but a few examples. A key challenge when using electrostatic classifiers, such as the CPMA or DMA, is the presence of multiply charged particles, which necessitates applying multiple charge correction methods to accurately account for all particles exiting the classifier [67, 196, 218].

For instance, recent work by Corbin et al. [36] employed CERMS to compare the Mass Absorption Cross Sections (MAC) of various soot sources. To quantify the size dependence of MAC, they developed a multiple charge correction methodology to estimate the average transmitted mass for a given CPMA mass-to-charge setpoint and unipolar charger operating condition. This is necessary because a distribution of masses exists

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downstream of the unipolar charger–PMA system: particles carrying multiple charges and correspondingly higher mass can be selected in the same way as singly charged particles. The mass distribution exiting the CPMA depends on the particle charge distribution—which is diameter-dependent rather than mass-dependent—and the CPMA transfer function [145, 182]. Accurately determining the average transmitted mass thus requires detailed knowledge of the aerosol, including the complex interrelationship between particle mass, mobility, and charge.

To address this, the iterative average charge (IAC) algorithm was developed. This algorithm estimates the average transmitted mass as the product of the CPMA mass-to-charge setpoint and the average transmitted charge. Implementing the IAC requires a charging model and an understanding of the mass-mobility relationship of soot particles [147, 49], allowing conversion between particle mass and diameter. Early sensitivity analyses revealed that uncertainties in the mass-mobility relationship led to a 20–30% margin of error in the algorithm’s estimates.

Building on this foundation, Sipkens et al. [180] introduced a more systematic approach to multiple charge correction for unipolar charger–PMA systems through the Interpolated Average Charge (INTAC) algorithm. INTAC advances the method by enabling real-time correction, explicitly formalizing assumptions about the average particle charge state. Specifically, it assumes that both the average particle charge and effective particle density can be parameterized by power law relationships as functions of mobility diameter, assumptions well supported by theoretical and experimental studies [42, 147, 142, 128, 199, 126]. By leveraging these relationships along with particle charging models, INTAC can predict the average transmitted mass through a unipolar charger–PMA system in real time via a straightforward and computationally efficient approach. This advancement facilitates the characterization of instrumentation using a mass-based metric. A numerical parametric study demonstrated that the algorithm achieves theoretical accuracy within  $\pm 20\%$ , despite variations in governing parameters such as aerosol morphology and the unipolar charger ion-time product ( $n_i t$ ).

Whilst the INTAC algorithm has been investigated numerically [180], there is no experimental evidence of how well the multiple charge correction methods work; the experimental assessment of the INTAC algorithm for determining the average transmitted mass from a power law model of charging and mass mobility is of particular interest due to the dependence of particle charging on particle morphology. It has been demonstrated that particle charging is material-independent [175] but can significantly depend on particle morphology [144, 176, 85, 153], with non-spherical particles charging between 10% - 30% higher than spherical particles of the same mobility diameter.

This work aims to experimentally validate the INTAC algorithm by measuring aerosols with a known spherical morphology (e.g. Dioctyl Sebacate (DOS)). Then, the method is

further probed by investigating a wide range of aerosols with varying particle morphologies. A slightly modified method for determining the CPMA speed and voltage required to select unipolar charged particles is introduced, demonstrating its applicability experimentally. Finally, a discussion on using a unipolar-charger-CPMA system to select particles monodisperse in mass is provided, focusing on how multiplying charging has consequences regarding the distribution of masses transmitted.

## 4.2 Multiple Charge Correction in Particle Mass Analysers

### 4.2.1 Theory

PMA select particles by their mass-to-charge ratio,  $s^*$ . The mass-to-charge ratio of the CPMA is given by

$$s^* = \frac{eV}{r_c^2 \omega_c^2 \ln\left(\frac{r_2}{r_1}\right)}, \quad (4.01)$$

where  $V$  is the classification voltage,  $e$  is electric charge carried by an electron,  $r_c$  is the radius of the centreline,  $\omega_c$  is the rotational speed at the centreline radius and  $r_1$  and  $r_2$  are the inner and outer radii of the classifier, respectively. Typically, when classifying aerosol particles, the classifier centroid describes the average particle property of interest. If the particles are all singly charged,  $s^* = m^* = \bar{m}$  and the mass-to-charge ratio and average mass are equivalent. However, if the particles are multiply charged due to unipolar charging, the average transmitted mass can be determined from [180, 36]

$$\bar{m} = s^* \bar{q} \quad (4.02)$$

where  $\bar{q}$  is the average charge of the transmitted particle population. The average transmitted charge can be determined through two methods. The first is direct parallel measurement downstream of the CPMA utilising an electrometer and a condensation particle counter (CPC) and is given by

$$\bar{q} = \frac{i}{NQ_a e} \quad (4.03)$$

where  $i$  is the measured current due to charge particles,  $N$  is the particle number concentration, and  $Q_a$  is the volumetric flow rate of the electrometer; this method requires two pieces of sampling instrumentation downstream of the CPMA. However, other methods are required when measurements from a CPC and electrometer are unavailable downstream. The INTAC algorithm requires no additional measurement downstream of the CPMA but

requires knowledge of the relation between mass, mobility, and charge. The INTAC starts by assuming that a power law can describe the average charge with respect to mobility diameter,  $d_m$

$$\bar{q} = q_0 d_m^v \quad (4.04)$$

where  $q_0$  is a pre-factor term and  $v$  an exponent.  $q_0$  and  $v$  can be obtained by fitting Equation 4.04 to either experimental measurements of the average charge against mobility diameter [199, 85, 172] or fitting to a numerical model such as that of Fuchs limiting sphere model. Fuchs [49] charging model predicts a nearly linear dependence between the average particle charge and equivalent charging diameter (*i.e.*,  $v = 1$ ). Experimental measurements typically predict an exponent between 1.0 - 1.2, which depends on several factors, including charger design and particle type [125, 199, 200, 173]. In the work of Sipkens et al. [180]  $q_0$  and  $v$  were found by fitting directly to Fuchs' law for  $\bar{q} > 4$ . Below this mean charge, the linear size dependence between average charge and diameter starts to break down. To further speed up computation and remove the need to repeatedly fit to Fuchs' model as the parameters were changed, Sipkens et al. [180] proposed a simplification for  $q_0$  given by

$$q_0 = [2.51 \times 10^{-18} (n_{it})^{2.1914}] \exp[-0.0316 \ln^2(n_{it})]. \quad (4.05)$$

where  $n_{it}$  is the ion-concentration time product characterising a unipolar charger's charging performance. Equation 4.04 can be substituted into Equation 4.02, but to solve for the average particle mass, the particle mass needs to be related to mobility diameter. This is typically done using another power law [42], where the particle mass is given by

$$m = \frac{\pi}{6} \rho_{\text{eff},100} d_{m,100}^{3-D_m} d_m^{D_m} = k d_m^{D_m}. \quad (4.06)$$

$\rho_{\text{eff},100}$  is the effective density of a 100 nm ( $d_{m,100}$ ) particle, providing a physical anchor point for the expression [147], and  $D_m$  is the mass-mobility exponent.  $D_m$  equals 3 for spherical particles and decreases as particles become more fractal. It is assumed that Equations 4.04 and 4.06 strictly pertain to average quantities, such that Equation 4.06 relates the average mass,  $\bar{m}$ , to the average mobility diameter,  $\bar{d}_m$ , by  $\bar{m} = k \bar{d}_m^{D_m}$ . This assumption is consistent with measurements derived from tandem classification using traditional analysis methods without data inversion [179, 224]. Consequently, Equation 4.06 can be used to convert Equation 4.04 into one that relates the average particle mass to the average particle charge, which can then be substituted into Equation 4.02 to determine the average particle mass.

$$\bar{m} = \left( k^{-\nu/D_m} q_0 s^* \right)^{\frac{D_m}{D_m-\nu}} \quad (4.07)$$

Equation 4.07 is referred to as the Power Law Average Charge (PLAC); it can be used in the multiple charge regime but breaks down in the single charge regime where  $\nu = 0$  and  $q_0 = 1$ . Sipkens et al. [180] therefore defined a simple function to interpolate between the single charge ( $s^* = \bar{m}$ ) and multiple charge regimes,

$$\bar{m} = \left[ (s^*)^n + (k^{-\nu/D_m} q_0 s^*)^{\frac{nD_m}{D_m-\nu}} \right]^{1/n}. \quad (4.08)$$

Equation 4.08 is the INTAC method where  $n$  governs the smoothness of transition between the single charge and power law charging regimes, taken as  $n = 2.5$  in this work. Equation 4.08 is derived based on a number of assumptions listed in the work of Sipkens et al. [180], which include neglect of the upstream mass distribution (*i.e.* assumed to uniform) and CPMA transfer function width, as well as assuming that the charge distribution on the transmitted particles is approximately the same as that for the average transmitted particle mass. Readers are referred to the work of Sipkens et al. [180] for a complete derivation of the INTAC algorithm. At a given CPMA mass-to-charge setpoint, the average transmitted mass is defined by four parameters: the charge pre-factor and exponent ( $q_0$  and  $\nu$ ) and mass-mobility pre-factor and exponent ( $\rho_{\text{eff},100}$  and  $D_m$ ).

The average charge of the transmitted aerosol calculated from the INTAC method can be determined by dividing Equation 4.08 by the mass-to-charge setpoint of the CPMA to give

$$\bar{q}_{\text{INTAC}} = \left[ 1 + (k^{-\nu/D_m} q_0)^{\frac{nD_m}{D_m-\nu}} (s^*)^{\frac{\nu n}{D_m-\nu}} \right]^{1/n}. \quad (4.09)$$

In this work, the mass distribution was not measured directly, nor was its average calculated. Instead, the average particle charge was measured downstream of the CPMA (Equation 4.03), and the mass was calculated using Equation 4.02. Since the average mass, regardless of the calculation method, is given by,  $s^* \bar{q}$ , the comparison is strictly between the average charge predicted by Equation 4.09 and the measured average charge. However, average masses are reported in the results section, which is functionally equivalent to reporting average charges. The average mass calculated using Equation 4.08 is referred to as the INTAC average mass, while the average mass calculated using the CPMA set-point and the measured average charge is referred to as the measured average mass.

### 4.2.2 Classification Resolution

Classification resolution is an important parameter that typically defines the width of the classifier transfer function at a given set point, where higher resolutions correspond to a narrower transfer function width. Numerical work demonstrated that the resolution parameter of the CPMA was found to have little impact on the INTAC algorithm [180]. However, the choice of resolution dictates the rotational speed and voltage at which the CPMA operates, which can influence the concentration of particles downstream of the CPMA. The resolution parameter,  $R_m$  of the CPMA is defined as [162]

$$R_m = \frac{m^*}{|m' - m^*|}, \quad (4.10)$$

where  $m^*$  is the nominal mass set-point of the CPMA and  $m'$  is the limiting particle mass. The limiting mass is the largest (or smallest) particle size (as the transfer function is assumed to be symmetric about  $m^*$ ) that will transmit through the CPMA. For a given mass set-point (*i.e.*, the mass of the particle that is intended to be selected,) and  $R_m$ , the limiting mass can be determined using Equation 4.10. The corresponding mobility diameter for both  $m^*$  and  $m'$  can be determined if mass-mobility constants  $\rho_{\text{eff},100}$  and  $D_m$  are known. From the mobility diameter, the mechanical mobility,  $B$ , can be calculated [70].

In calculating the resolution of the CPMA transfer function, it is typically assumed that the particles are singly charged. However, in this use case, since the particles are unipolarly charged, a model is required to determine the charge acquired by a particle of a given size. Here, the model proposed by White [217] is used, which is an analytically solvable equation for the mean charge on an aerosol when combining field and diffusion charging. The result of which is given by

$$\bar{q} = \frac{d_m k_b T}{2K_E e^2} \ln \left( 1 + \frac{\pi K_E d_m \bar{c}_i e^2 n_i t}{2k_b T} \right) + \frac{3\epsilon}{\epsilon + 2} \frac{E d_m^2}{4K_E e} \frac{\pi K_E e Z_i n_i t}{1 + \pi K_E e Z_i n_i t} \quad (4.11)$$

where  $K_E = 1/(4\pi\epsilon_0)$  and  $\epsilon_0$  is the permittivity of a vacuum,  $\bar{c}_i$  is the mean thermal speed of the ions,  $E$  is the electric field strength within the charging region and  $k_b$  and  $T$  are the Boltzmann constant and temperature respectively. It is assumed that, at each particle size, the charge distribution is infinitesimally narrow, such that the probability of a particle attaining any charge other than its mean is zero. Whilst this is clearly not the case for real chargers in which a distribution of charges exists, this assumption enables rapid calculation of the CPMA speed and voltage profile. The analytical model of White could readily be replaced by a power law representation, as given by Equation 4.04, that better reflects experimental measurements

of the average charge of a particle as a function of size, allowing more flexibility for different particle types. However, these may have to be measured on a particle-by-particle basis.

The equations for approximating the CPMA resolution proposed by Reavell et al. [162] can be solved to find the voltage given by

$$V = \frac{Q_a \ln\left(\frac{r_2}{r_1}\right)}{2\pi B' L e q} \cdot \frac{1}{\frac{m'}{m} - \frac{q'}{q}} \quad (4.12)$$

and the rotational speed, which is given by

$$\omega = \left( \frac{eqV}{r_c^2 \ln\left(\frac{r_2}{r_1}\right)} \right)^{\frac{1}{2}}. \quad (4.13)$$

Note that if  $q = q' = 1$ , the voltage and speed correspond to the singly charged case. To distinguish between the two methods in this work,  $R_{m,+1}$  defines the resolution calculated assuming particles acquire only a single charge (*i.e.*  $q = q' = 1$ ), and  $R_{m,q}$  as the resolution considering that the particles have been unipolarly charged (*i.e.*  $q$  and  $q'$  are calculated from Equation 4.11). A comparison of the speed and voltage profile of the CPMA as a function of the nominal mass-set point (*i.e.* the target particle mass) is given in Figure 4.1. The rotational speeds are similar between the two methods, as the nominal particle mass to be selected is the same in both instances; however, the voltages in the multiple charge case are significantly lower at larger particle sizes owing to the multiple charges acquired on the particles. Convergence of the voltages between the two calculation methods occurs at smaller particle sizes where even unipolarly charged particles can obtain at most one charge. A kink is present in the  $R_{m,q}$  voltage at smaller masses, representing the point at which the average particle charge first increases above 1. There are two main benefits to utilising this calculation ( $R_{m,q}$ ) of the speed and voltage rather than the single charge case. Firstly, assuming particles are singly charged leads to a significant discrepancy between the selected particle mass and the actual average transmitted mass, which can complicate experiments to some extent. Secondly, since the CPMA voltage limit (1000 V) is not reached, the upper particle size limit is extended well beyond 1  $\mu\text{m}$ . As will be demonstrated, this allows for significantly higher current and number concentrations downstream of the CPMA when selecting particles with the same average mass, thereby improving the signal-to-noise ratio.

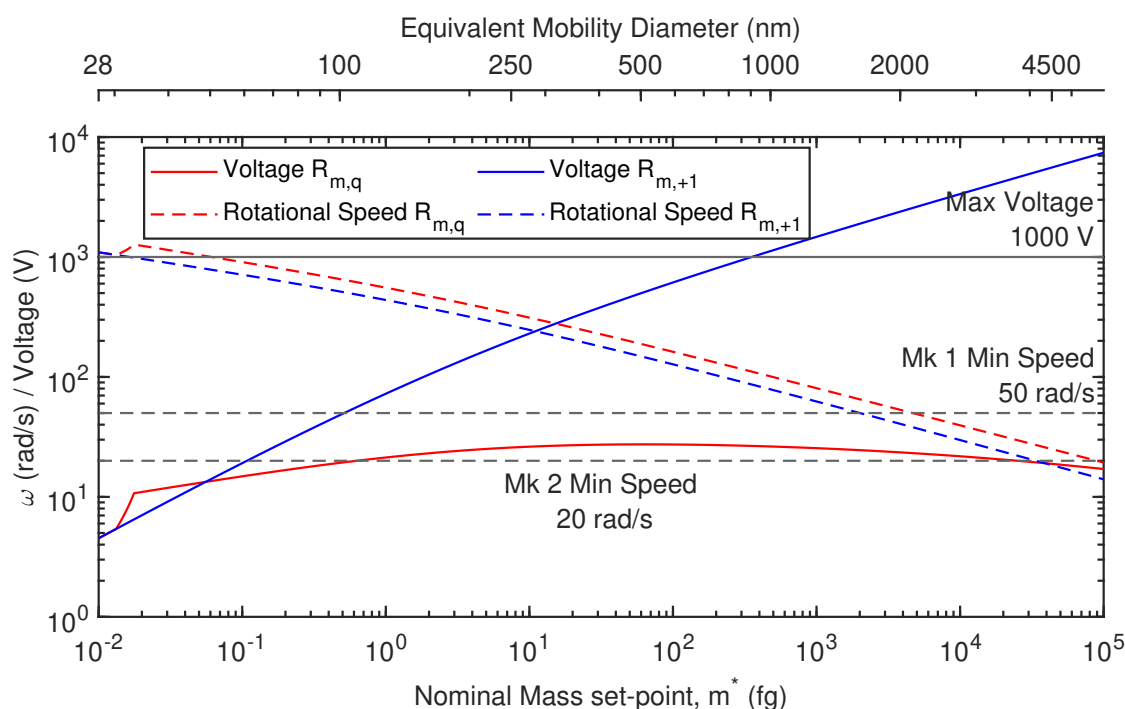


Fig. 4.1 Comparison of the CPMA rotational speed and voltage profile for singly charged particles ( $R_{m,+1}$ ) and for multiply charged particles ( $R_{m,q}$ ). The profile is derived for an  $n_{it}$  product of  $4 \times 10^{13} \text{ s m}^{-3}$  and for spherical DOS with a density equal to  $913 \text{ kg m}^{-3}$ . Note also indicated in the Figure is the maximum voltage (1000 V) and minimum rotational speed ( $50 \text{ s}^{-1}$ ) of the Mk1 CPMA, which limit the particle masses which can be selected.

## 4.3 Experimental Methodology

### 4.3.1 Experimental Set-up

The experimental set-up to validate the INTAC algorithm is shown in Figure 4.2. Particles of a variety of compositions and morphologies were generated using multiple aerosol generation equipment. Water-soluble aerosols of Sodium Chloride (NaCl) and Nigrosin were generated by atomising a 1% w/v solution in de-ionised water using a TSI 9026 atomiser. After atomisation, any large mobilised liquid droplets were removed in a liquid trap, and the aerosol stream was subsequently dried in a diffusion dryer. The relative humidity downstream of the drier was confirmed to be less than 15% using an RH sensor (Sensirion SHT-85). Dioctyl Sebacate (DOS) was generated using a Collison nebuliser; the diffusion dryer was bypassed in this case. In addition to generation by atomisation, NaCl particles were also produced by an evaporation-condensation process using the Silver Particle Generator (SPG, Catalytic Instruments) [64]. The SPG was operated with a primary flow rate of  $2 \text{ L min}^{-1}$  and

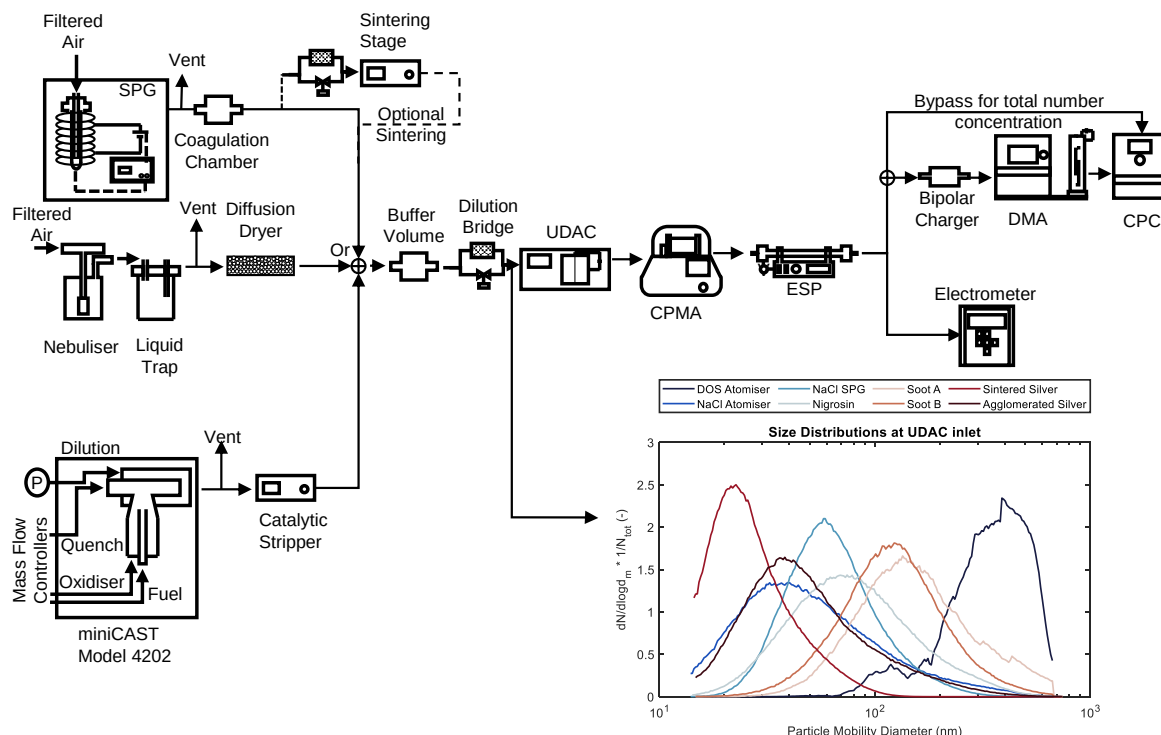


Fig. 4.2 Experimental set-up used to validate the INTAC algorithm using various aerosol sources. The inset Figure shows the particle mobility size distributions of the various aerosols at the inlet to the UDAC measured using an SMPS.

a temperature of  $750\text{ }^{\circ}\text{C}$ . The dilution flow of the SPG was set to  $10\text{ L min}^{-1}$ . Silver particles were also generated in the SPG at a temperature of  $1100\text{ }^{\circ}\text{C}$ , a primary flow rate of  $2\text{ L min}^{-1}$ , and no dilution flow was used. Optionally, the flow was passed through a sintering stage to compact the silver particles into spheres. The sintering stage (S8000 Particle Sintering Stage, Catalytic Instruments) was operated at a temperature of  $550\text{ }^{\circ}\text{C}$ .

Soot particles were generated using a miniCAST model 4202 (Jing Ltd., Switzerland) with two oxidiser-to-fuel ratios, henceforth referred to as Soot A and Soot B. The miniCAST burner is a co-flow, laminar diffusion flame generator consisting of a coaxial inner tube for the fuel gas stream and an outer annular region supplying dry, particle-free oxidant air. This design enables stable, repeatable generation of carbonaceous aerosol, with particle properties tunable via adjustments to the fuel–air ratio, quench gas dilution, and other operating parameters [130]. For both Soot A and B, the fuel flow rate, dilution pressure and quench gas remained fixed at  $0.06\text{ L min}^{-1}$ , 3 bar and  $7.5\text{ L min}^{-1}$ , respectively. The oxidation air flow rate for Soot A was  $1.4\text{ L min}^{-1}$  and Soot B was  $1.8\text{ L min}^{-1}$ . The variation in fuel to oxidiser changes the soot morphology produced, as demonstrated by the comprehensive

evaluation of the miniCAST by Moore et al. [130]. A catalytic stripper (CS015, Catalytic Instruments) removed any semi-volatile material.

After generation, all aerosols were passed through a buffer volume to ensure adequate mixing, and a dilution bridge was used to adjust the aerosol concentration. This was done to reduce the aerosol concentration to prevent ion saturation in the charger which can adversely affect the charging process.

Table 4.1 summarises the aerosols utilised and the assumed parameters used to determine the average transmitted mass using Equation 4.08. It is assumed that all aerosols charge in the same manner such that the charging law parameters,  $q_0$  and  $v$ , are identical for each aerosol.

Table 4.1 Power law coefficients of Equations 4.04 and 4.06 used to determine the average transmitted mass as a first guess for each aerosol. Each aerosol is assumed to follow a charging power law modelled by Fuchs [49] where  $v = 1$  and  $q_0$  is given by Equation 4.05 for an  $n_{it} = 4 \times 10^{13} \text{ s m}^{-3}$ . Therefore,  $v$  and  $q_0$  are assumed to be the same for each material. Where particles are assumed to be spherical ( $D_m = 3$ ),  $\rho_{\text{eff},100}$  is equal to the bulk density of the material. The mass-mobility of other materials is taken from literature values where available.

| Aerosol                | $q_0$  | $v$ | $\rho_{\text{eff},100} (\text{kg m}^{-3})$ | $D_m$ |
|------------------------|--------|-----|--------------------------------------------|-------|
| DOS                    |        |     | 913                                        | 3     |
| NaCl *                 |        |     | 1900                                       | 2.934 |
| Nigrosin †             | 0.0556 | 1   | 1632                                       | 3     |
| Soot ‡                 |        |     | 510                                        | 2.48  |
| Sintered Silver        |        |     | 10490                                      | 3     |
| Agglomerated Silver ** |        |     | 2017                                       | 2.07  |

\* Mass-mobility of NaCl assuming a cubic structure [155, 229]

† Mass-mobility of Soot taken as equal to values given by the universal soot relation [147].

‡ Nigrosin is assumed spherical with a density determined by [208]

\*\* Mass-mobility values of Agglomerated Silver from the SPG have not been investigated in the literature. Here, values from Kim et al. [94] are used who generated particles with a tube furnace at similar temperature conditions to the SPG used in this study.

After generation and dilution, particles were passed through a Unipolar Aerosol Diffusion Charger (UDAC Mk2, Cambustion Ltd.). The UDAC operates by using a fine wire held at a controlled voltage to generate ions in air. These highly mobile ions are transported into the charger's charging region by an alternating electric field, where they transfer their charge to the aerosol particles. A detailed description of the UDAC can be found in Biskos et al. [20]. For DOS measurements, three  $n_{it}$  products were investigated,  $4 \times 10^{12} \text{ s m}^{-3}$ ,  $1 \times 10^{13} \text{ s m}^{-3}$ ,  $4 \times 10^{13} \text{ s m}^{-3}$ . All other aerosols were only investigated at an  $n_{it}$  of  $4 \times 10^{13} \text{ s m}^{-3}$  as

this minimises any undue effects of uncharged particles and increases the electrometer signal as particles acquire more charge. Particles were then selected using a CPMA (Mk1, Cambustion Ltd.). The CPMA was run at a resolution between 3 - 5 for all measurements as defined in Section 4.2.2. Unless otherwise stated, this resolution refers to the multiple charge calculation method ( $R_{m,q}$ ). After classification, the aerosol was passed through an electrostatic precipitator (ESP, Cambustion Ltd.). The ESP was used to quantify the number of uncharged particles at a given CPMA set point. When the ESP is turned on (2000 V), the number of neutrally charged particles,  $N_0$  can be quantified. To reduce the effect of uncharged particles on measurements, only data in which the fraction of uncharged particles,  $f_0 = N_0/N$  where  $N$  is the total aerosol concentration measured with the ESP turned off, was less than 5% was included in subsequent analysis. The flow downstream was then split between a 3752 CPC (TSI Inc., USA) and a 3086B electrometer (TSI Inc., USA) operated at flows of  $\sim 0.3 \text{ L min}^{-1}$  and  $\sim 1.39 \text{ L min}^{-1}$ , respectively. In addition to a criterion on the fraction of uncharged particles, electrometer data was only accepted if the total current was greater than 50 fA. The mean charge measurements were accompanied by mobility distribution measurements of the CPMA classified distribution, measured using an SMPS system consisting of a bipolar charger (TSI Inc., USA), a 3081 DMA (TSI Inc., USA) operating at a sheath to aerosol flow rate of 10:1 followed by a CPC. Two mobility distribution measurements were taken per CPMA classification set-point. The mobility distribution was used to determine the average particle mobility diameter,  $\overline{d_m}$ , downstream of the CPMA. This average mobility diameter was used to evaluate the average particle charge as a function of mobility size as well as determine the average particle effective density through

$$\overline{\rho_{\text{eff}}} = \frac{6\overline{m}}{\pi\overline{d_m}^3} = \frac{6s^*\overline{q}}{\pi\overline{d_m}^3}. \quad (4.14)$$

For the experimental measurements, the definition of mean charge is slightly altered from that given in Equation 6.14. First, a counting efficiency term,  $\eta$ , is included, which accounts for any differences between the electrometer's and CPC's counting efficiencies. This was measured using a tandem CPMA-DMA set-up as described in Song et al. [184] and was found to be  $1.01 \pm 0.03$ . Secondly, only the charged particles are of interest; therefore, the concentration of uncharged particles is taken into account. The mean charge is, accordingly, given by

$$\overline{q} = \frac{i}{\eta (N - N_0) Q_a e}. \quad (4.15)$$

Note that this correction has minimal effect on the results as only data in which the neutral fraction is less than 5% was utilised in subsequent analysis.

### 4.3.2 Experimental Uncertainty

Uncertainty is categorised into two primary types: Type A and Type B [1]. Type A uncertainty is evaluated through statistical analysis of repeated measurements and, in this work, is expressed as the standard deviation of the mean. This corresponds to the standard deviation over a period of at least 90 s for mean charge measurements.

Type B uncertainty, on the other hand, accounts for systematic errors associated with the measurement instruments. Often referred to as bias uncertainty, it is typically determined from manufacturer-specified uncertainty values or through theoretical and experimental equipment analysis. This work takes the uncertainty in CPC concentration as 5% [204]. The uncertainty in electrometer current is defined as the greater of either 2% or 5 fA, depending on the specific measurement and the uncertainty in the electrometer flow rate is 2% [203]. Additionally, the CPMA and DMA classification set-point uncertainty are taken as 2.7% and 3.3%, respectively [191, 96]. The total uncertainty is obtained through propagation of error by combining Type A and Type B uncertainties using the root sum of squares method, assuming they are independent sources of error.

## 4.4 Results and Discussion

### 4.4.1 Comparison of distributions obtained from singly charged and multiply charged CPMA speed and voltage profiles

Figure 4.3 compares the measured particle concentrations and particle currents downstream of the CPMA for the two different resolution definitions,  $R_{m,+1}$  and  $R_{m,q}$ , for scan profiles with a target resolution of 3. Below  $\sim 10$  fg (275 nm mobility size for DOS particles), the two methods provide similar particle concentrations and currents. This is because, at smaller particle sizes, the relative difference in integer charge states is larger (*i.e.*,  $q = 1, 2, 3, \dots$ ), which means a broader range of masses is transmitted through the CPMA. Therefore, the charge distribution width is the driving parameter for the mass distribution of particles transmitted rather than classifier resolution (Section 4.4.5 discusses this in more detail). However, above this size, a divergence occurs, in which both the measured concentrations and currents significantly decrease as the mass increases when utilising the single charge resolution profile for the CPMA speeds and voltages ( $R_{m,+1}$ ). For the single charge case, the voltage in the CPMA increases significantly as the mass increases (see Figure 4.1). Due to the high charge on the aerosol, the high voltage in the classification section of the CPMA results in significant electrostatic precipitation of the highly charged particles. Whereas with the multiple charge profile, the voltage is significantly reduced to account for the higher aerosol

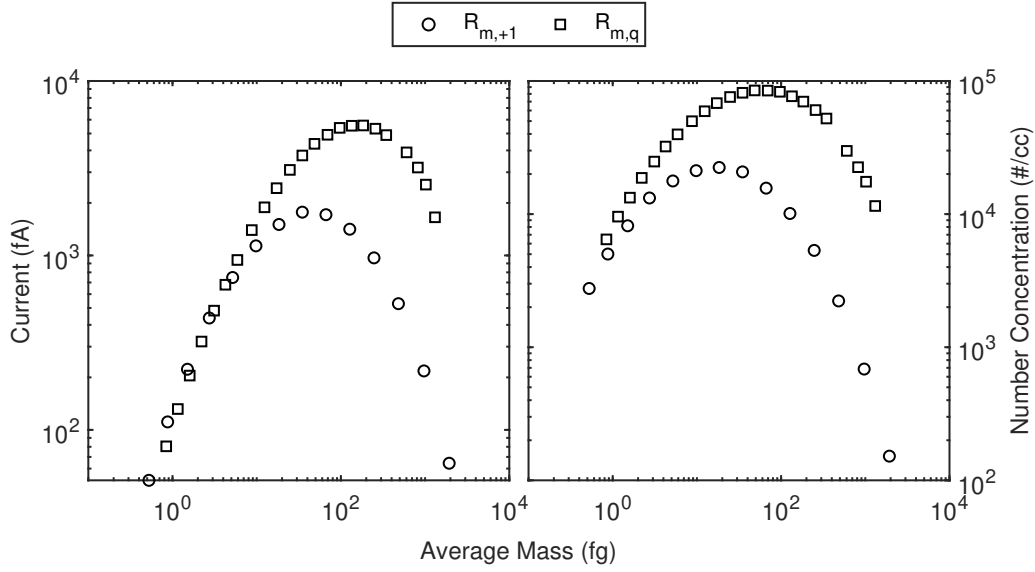


Fig. 4.3 Demonstration of the effect of CPMA speed and voltage profile calculation ( $R_{m,+1}$  and  $R_{m,q}$ ) on the experimentally measured particle concentration and current for DOS particles at an  $n_{it} = 4 \times 10^{13} \text{ s m}^{-3}$  as a function of average transmitted particle mass ( $s\bar{q}$ ). The operational speed and voltage set-points of the CPMA were calculated as detailed in Section 4.2.2 with a target resolution of  $R_{m,+1} = R_{m,q} = 3$ .

charge state, which dramatically extends the operating range of the CPMA when paired with a unipolar charger whilst maintaining a high signal-to-noise ratio, enabling measurements well above  $1 \mu\text{m}$ . Note in Figure 4.3 that the upper mass is limited by the minimum rotational speed of the classifier, which is  $50 \text{ rad s}^{-1}$ . The minimal rotational speed of the newer CPMA Mk2 model is as low as  $20 \text{ rad s}^{-1}$ , which would enable measurements at even higher masses. Furthermore, the rotational speed floor of the CPMA can be circumvented by operating the CPMA at higher resolutions for the same nominal mass set-point. The CPMA can, therefore, be operated to at least  $3 \mu\text{m}$  with the multiply charged scan profile. The increase in current signal at larger sizes using the multiple charge resolution definition will benefit any measurements that use an electrometer downstream of the CPMA, such as CERMS [191].

#### 4.4.2 Validation with Spherical particles

Due to their known spherical morphology, DOS particles were chosen to validate the INTAC methodology at different  $n_{it}$  products. These results are shown in Figure 4.4. Figure 4.4a shows the percentage error between the INTAC calculated mass and the measured average mass, whilst Figure 4.4b shows the comparison of the INTAC mass with the measured average mass on a log-log scale. The INTAC algorithm performs well (within  $\pm 20\%$ ) below

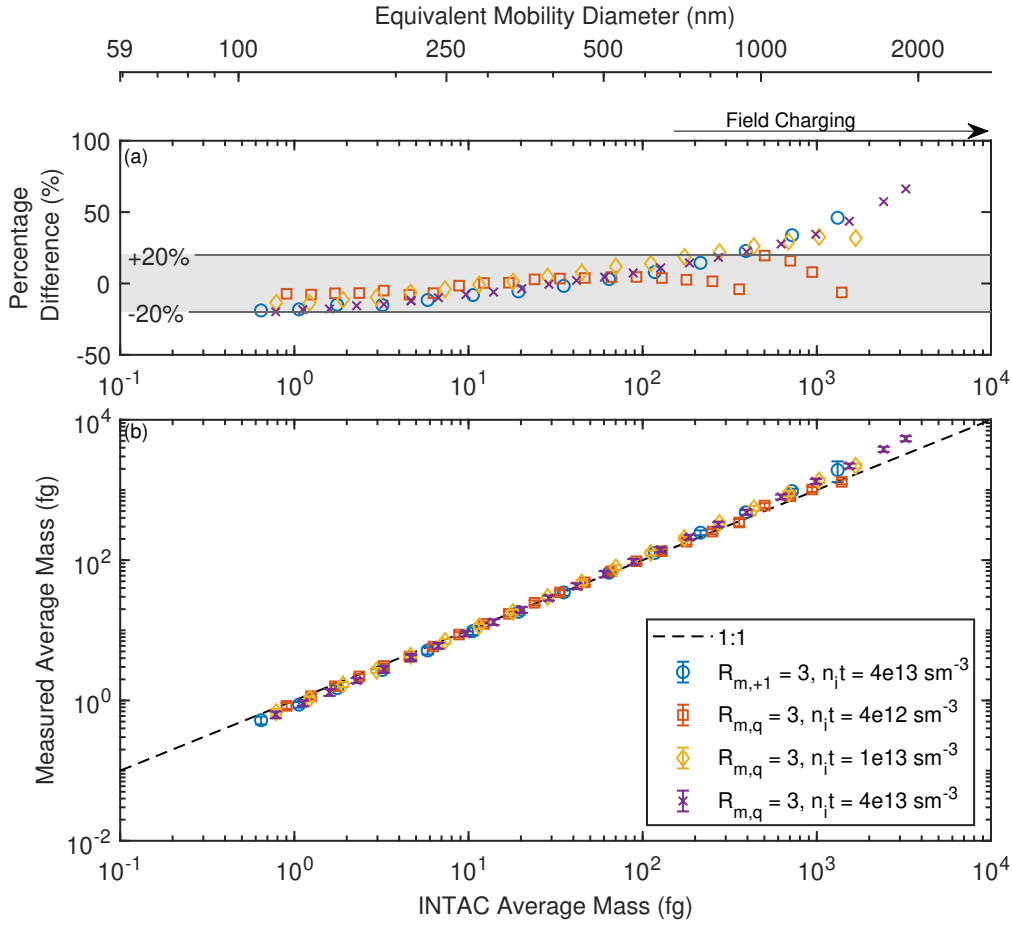


Fig. 4.4 Comparison of the INTAC average Mass (Equation 4.08) to the experimentally determined average mass (Determined by combining Equations 4.02 and 4.15) for DOS particles. (a) shows the percentage difference between the two methods, and (b) compares the INTAC and measured average mass on a log-log scale. The equivalent mobility diameter is calculated from the INTAC average mass assuming spherical particles with a bulk density of  $913 \text{ kg m}^{-3}$

$\sim 500 \text{ nm}$  for a range of  $n_i t$  products, also showing extremely similar results when utilising two different resolution profiles,  $R_{m,+1}$  and  $R_{m,q}$  at an  $n_i t$  of  $4 \times 10^{13} \text{ s m}^{-3}$ , suggesting the resolution profiles make minimal difference to the INTAC algorithm. The average absolute percentage difference between the measured and INTAC-predicted average mass for all measurements is  $13.43\% \pm 12.66\%$ , which improves to  $8.09\% \pm 5.45\%$  for particles below  $100 \text{ fg}$  (the number after the  $\pm$  indicates  $1\sigma$  from the mean). Above  $\sim 500 \text{ nm}$ , the measured average mass is larger than the INTAC predicted mass for both  $n_i t$  values of  $1 \times 10^{13} \text{ s m}^{-3}$  and  $4 \times 10^{13} \text{ s m}^{-3}$ . This is likely due to field charging, as the Figure indicates. A square-wave electric field is applied within the charging region of the UDAC to pull ions through a

grounded grid [20], and therefore, the aerosol is subject to some amount of field charging. Field charging is proportional to  $d_m^2$  and, therefore, becomes the more dominant mode of charging for larger particles [70]. The coefficients of  $q_0$  and  $v$  of the INTAC algorithm are derived from fitting to Fuchs' theory [49], a model solely based on diffusion charging, which neglects any additional charge gained from an external electrical field. Note that the INTAC model could be readily extended to model field charging, as field charging can also follow some functional power law [150]. However, the power law charging model may require separation into a diffusion and field charge regime, which would be size dependent, as in other electrical-based classification methods such as the Electrical Lower Pressure Impactor (ELPI) [76, 150]. Due to the potential influence of field charging, the results in the following sections only include particles up to  $\sim 500$  nm in mobility equivalent size.

#### 4.4.3 Validation with a variety of different aerosol composition and morphology

Further validation of the INTAC algorithm has been performed for various aerosols with a comparison of the INTAC predicted mass to the measured average mass shown in Figure 4.5, with INTAC average mass values calculated using the assumed charge and mobility parameters given in Table 4.1. The general trend exhibited across the range of aerosols investigated is that the INTAC calculated mass compares better to the measured average mass for compact aerosols. This is particularly clear when comparing particles of the same composition but with different generation methods (e.g., NaCl atomised vs NaCl evaporation condensation or sintered vs. agglomerated silver), producing aerosols with vastly different morphologies. The improved performance of the INTAC model in predicting the average transmitted mass of compact or spherical aerosols is expected, as greater confidence is held in the mass–mobility relationship of these aerosols and their behaviour in unipolar charging systems. The average absolute difference between the INTAC algorithm and the measured mass for compact aerosol (DOS, Nigrosin, atomised NaCl and sintered silver are considered compact, confirmed through measurement of their effective density (see Figure 4.6c)) is  $9.06\% \pm 8.1\%$ . Whereas for the remaining four aerosols (SPG NaCl, Soot A and B and Agglomerated Silver), which are non-spherical (see Figure 4.6c), the average absolute difference is  $96.5\% \pm 74.2\%$ . This mainly stems from errors in the mass-mobility relation, as the mass-mobility of agglomerated silver and NaCl produced from the SPG are entirely unknown, given that the SPG is relatively new [64], and as such, there is minimal literature on the morphology of particles produced from the generator. This introduces significant errors ( $> 100\%$ ) in the INTAC average mass calculation, and, as will be shown in the Section 4.4.4,

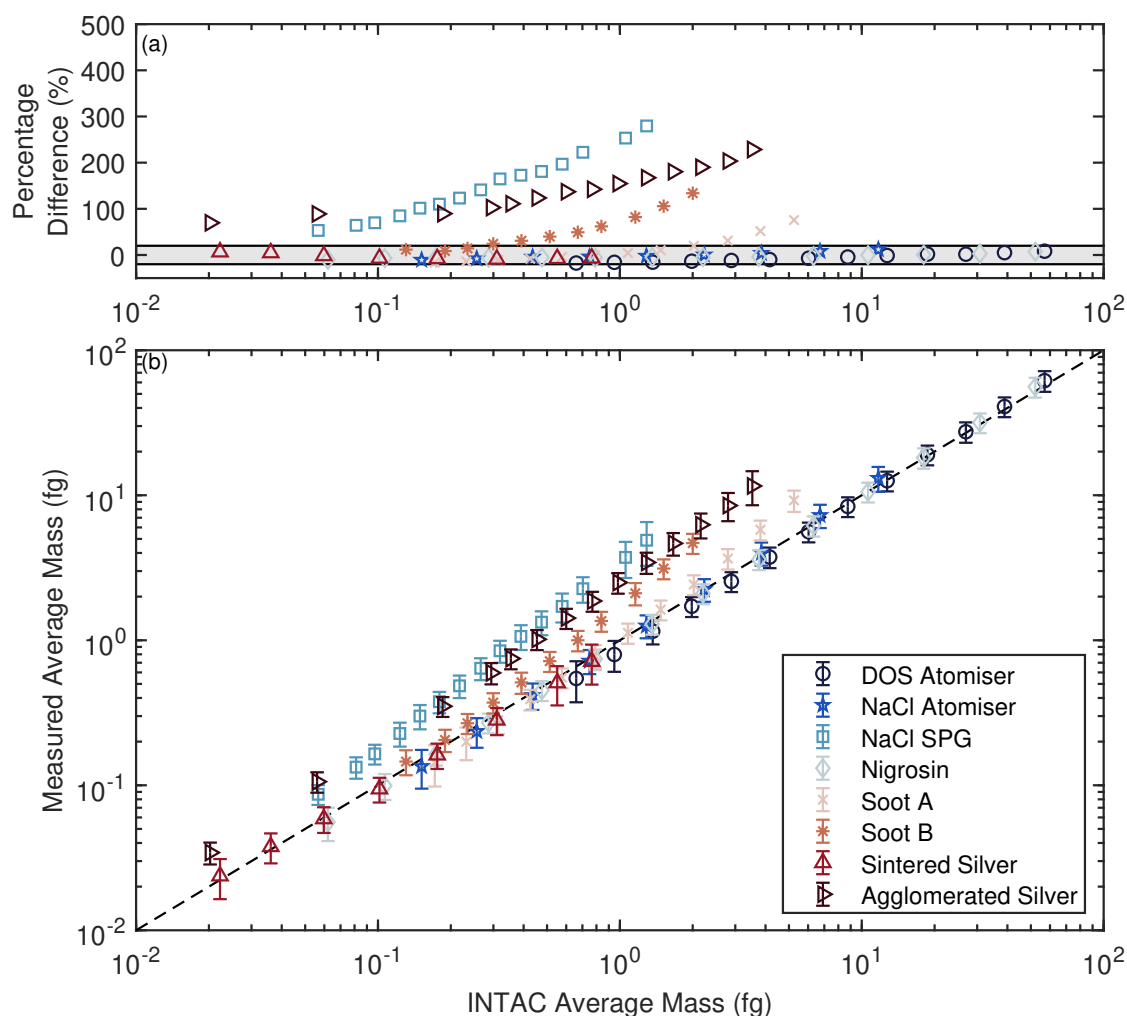


Fig. 4.5 Comparison of the INTAC average Mass (Equation 4.08) to the experimentally determined average mass (Determined by combining Equations 4.02 and 4.15) for a variety of aerosols indicated in the legend. Figure (a) shows the percentage difference between the two methods, and Figure (b) compares the average mass of the INTAC method with the measured mass on a log-log scale. The grey shaded region in Figure (a) indicates a  $\pm 20\%$  error.

correcting the mass-mobility relation dramatically reduces the errors. However, it should be noted even for an aerosol such as soot for which a better estimate of the mass-mobility relation exists [147], there is still a reasonable degree of error,  $35.17 \pm 35.5\%$ , which again revolves around uncertainty in both the charge and mass-mobility of the aerosol.

As errors between the INTAC predicted average mass and the measured average mass stem from differences in both the models used to predict the average charge as a function of particle size and the mass-mobility relation [182], it is useful to compare and contrast

the properties in Table 4.1 to those obtained experimentally. A comparison of the measured average charge and that predicted using Equation 4.04 evaluated with a  $q_0 = 0.0556$  and  $\nu = 1$  are shown in Figures 4.6 a and b. Figure 4.6a shows the percentage difference between predicted and measured average charge, and Figure 4.6b shows the average charge as a function of mobility diameter on a log-log scale. As expected, the predicted charge compares well to the measured average charge for compact aerosols of DOS, Nigrosin, atomised NaCl and Sintered Silver with an average absolute difference of  $6.95\% \pm 5.61\%$ . There is a slightly larger discrepancy between the measured average charge relative to the predicted average charge for sintered silver particles; however, this stems from the power law fit to Fuchs' charge model, which is used to determine  $q_0$  and  $\nu$ . In the work of Sipkens et al. [179], fitting directly to Fuchs' model is only performed for  $\bar{q} > 4$ . For mean charges lower than this, extrapolating the power law fit results in differences between Fuchs' charging model and the power law fit.

The absolute average difference between the predicted and measured charges for the agglomerate structures exhibited by soot, agglomerated silver and NaCl produced in the SPG is  $15.46\% \pm 8.84\%$ . This finding is in extremely good agreement with the existing literature [85, 176, 144, 153], which has found agglomerates typically charge between 10% - 30% more than spherical particles of the same mobility size. An increase in the average charge acquired relative to the predicted charge linearly propagates to the predicted average mass. Therefore, if agglomerated aerosols attain 10–30% more charge, the actual average transmitted mass will exceed INTAC algorithm predictions by the same margin, (discounting any uncertainty in the mass-mobility relation).

The differences between the proposed power law and experimental measurements can be remedied by directly fitting Equation 4.04 to the experimental data. Values of  $q_0$  and  $\nu$  are tabulated in Table 4.2. With the exception of sintered silver, aerosols have charge power law exponents between 1.05 and 1.2, similar to previous experimentally measured values [199, 125, 85, 13]. Sintered silver has a lower exponent as the data points lie in the transition between the singly charged ( $\bar{q} = 1$ ) and power law charge regimes ( $\bar{q} > 4$ ).

The experimentally determined effective density of each aerosol is shown in Figure 4.6c along with black-dashed lines indicating the effective density relations used for the INTAC algorithm as described in Table 4.1. Spherical aerosols of Nigrosin, DOS, and sintered silver closely follow the expected effective density relations. Atomised NaCl aerosol follows the cubic relation relatively closely, although the NaCl particles in this study are slightly less cubic (lower effective density), which is likely due to the drying rate, which directly affects the particle morphology [229, 216]. The effective densities of both soot aerosols are reasonably consistent with the universal soot relation with errors of 20% at the anchoring

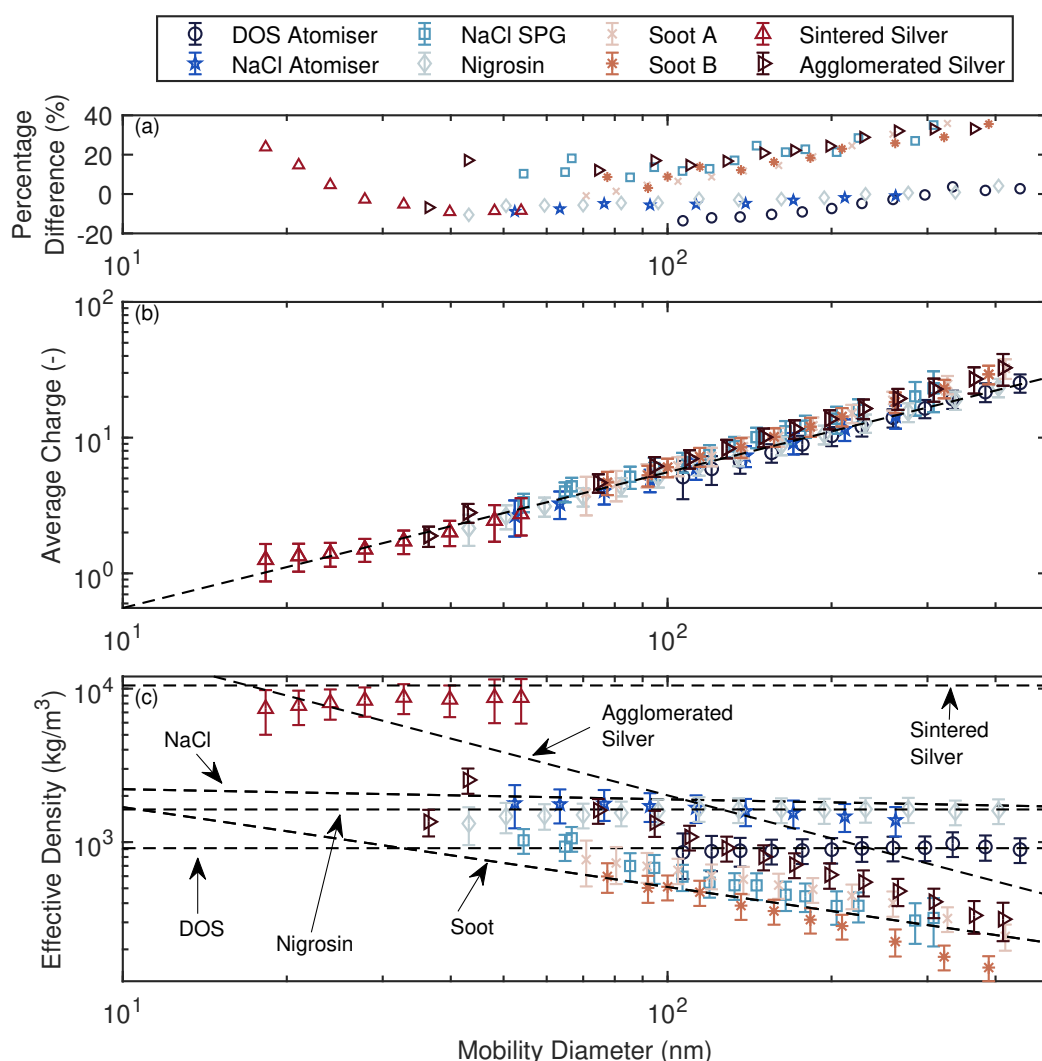


Fig. 4.6 Experimental measurements of average charge and effective density for the aerosols summarised in the legend. (a) shows the percentage difference between the measured average charge and the predicted average charge (Equation 4.04 with  $q_0 = 0.0556$  and  $\nu = 1$ ) as a function of particle mobility diameter. (b) shows the average charge as a function of mobility diameter on a log-log scale. The black dashed line in Figure (b) is the average charge predicted using Equation 4.04. (c) shows the effective density calculated using Equation 4.14. Black dashed lines indicate the effective densities detailed in Table 4.1 for comparison to the experimental data. Each effective density is labelled with the aerosol it corresponds to in the Figure.

point of the relation at 100 nm. However, larger discrepancies exist away from the anchoring point, suggesting errors in the density exponent.

NaCl and Silver produced from the SPG, without downstream altering through sintering, produce highly agglomerated aerosols and, as such, have effective densities much lower

than those predicted using the given parameterisations. The agglomerated NaCl and Silver produced by the evaporation-condensation technique significantly differ from assumed mass-mobility relations, leading to the extremely large errors shown in Figure 4.5a.

To better illustrate the difference between the assumed mass-mobility parameters and those used to evaluate the INTAC algorithm (Table 4.1), Equation 4.06 can be fit to the experimental data to obtain values for  $\rho_{\text{eff},100}$  and  $D_m$ . These are summarised in Table 4.2.

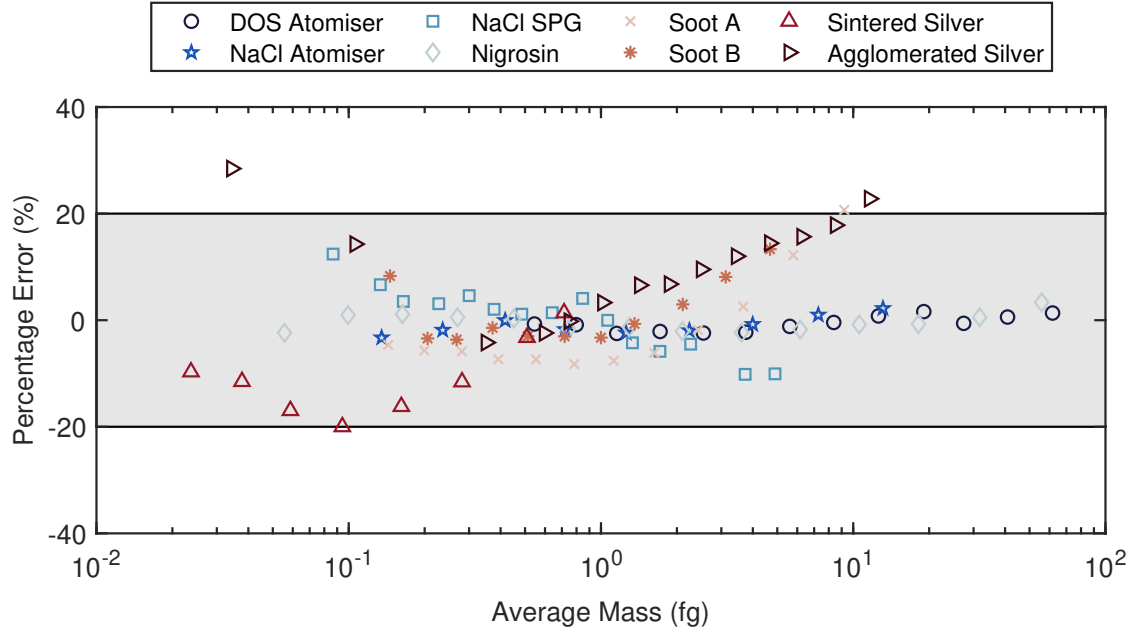


Fig. 4.7 Percentage error between measured mass and INTAC mass evaluated using the experimentally determined values of  $q_0$ ,  $v$ ,  $\rho_{\text{eff},100}$  and  $D_m$  given in Table 4.2.

#### 4.4.4 Correction of INTAC properties to experimental data

The difference between the experimentally measured charge and mass-mobility relations shown in Figure 4.6 compared to those assumed in Table 4.1 result in errors in the INTAC-determined average mass. The INTAC algorithm can be re-evaluated to determine the average mass using the values of  $q_0$ ,  $v$ ,  $\rho_{\text{eff},100}$  and  $D_m$  in Table 4.2. This reevaluation is shown in Figure 4.7. These results verify that the INTAC method works well (average absolute difference of  $5.64 \pm 5.72$ ) across a wide range of aerosols and masses (0.01 fg to 100 fg) when each aerosol's charge and mass-mobility relations are experimentally determined.

Table 4.2 Power law coefficients of Equations 4.04 and 4.06 obtained from least squares fitting to experimental data. Numbers in brackets indicate a 95% Confidence interval from least squares fitting to the experimental data shown in Figure 4.6.

| Aerosol             | $q_0$                   | $\nu$                   | $\rho_{\text{eff},100} \text{ (kg m}^{-3}\text{)}$ | $D_m$                 |
|---------------------|-------------------------|-------------------------|----------------------------------------------------|-----------------------|
| DOS                 | 0.0267 ( $\pm 0.0038$ ) | 1.13 ( $\pm 0.0241$ )   | 865 ( $\pm 28$ )                                   | 3.05 ( $\pm 0.033$ )  |
| Nigrosin            | 0.0347 ( $\pm 0.003$ )  | 1.131 ( $\pm 0.0128$ )  | 1542 ( $\pm 42$ )                                  | 3.06 ( $\pm 0.036$ )  |
| NaCl Atomsier       | 0.0422 ( $\pm 0.0022$ ) | 1.048 ( $\pm 0.0099$ )  | 1666 ( $\pm 31$ )                                  | 2.84 ( $\pm 0.036$ )  |
| NaCl SPG            | 0.0347 ( $\pm 0.0074$ ) | 1.138 ( $\pm 0.0396$ )  | 671 ( $\pm 31$ )                                   | 2.23 ( $\pm 0.099$ )  |
| Soot A              | 0.0235 ( $\pm 0.0024$ ) | 1.2 ( $\pm 0.0176$ )    | 659 ( $\pm 21$ )                                   | 2.45 ( $\pm 0.0751$ ) |
| Soot B              | 0.0286 ( $\pm 0.0035$ ) | 1.16 ( $\pm 0.0217$ )   | 495 ( $\pm 16$ )                                   | 2.21 ( $\pm 0.0712$ ) |
| Sintered Silver     | 0.1178 ( $\pm 0.0511$ ) | 0.7818 ( $\pm 0.1188$ ) | 9716 ( $\pm 822.8$ )                               | 3.14 ( $\pm 0.0712$ ) |
| Agglomerated Silver | 0.0325 ( $\pm 0.0062$ ) | 1.14 ( $\pm 0.033$ )    | 1084 ( $\pm 206$ )                                 | 2.35 ( $\pm 0.249$ )  |

#### 4.4.5 Mass selection of particles: The width of the classified mass distribution

Classifiers are often used to select particles of a given property to evaluate downstream instrumentation. In this use case, the width of the classified distribution is important, as ideally, the classified distribution is monodisperse (often considered to be geometric standard deviation,  $\sigma \leq 1.2$ ). The classifier resolution governs the width of the classified distribution. In the particular case of a unipolar charger-CPMA system, the mass resolution of the transmitted particles includes contributions from the unipolar charger and the CPMA. To demonstrate how the width of the transmitted distribution varies with particle mass, a numerical model was employed, as described in Sipkens et al. [179], in which the unipolar charger is represented using the framework of Fuchs [49], and the CPMA transfer function is characterised based on the work of Sipkens et al. [182]. The mass–mobility properties of DOS listed in Table 4.1 were assumed, along with a charger ion exposure ( $n_i t$ ) of  $4 \times 10^{13} \text{ s m}^{-3}$ . These parameters are relatively arbitrary, and similar conclusions can be drawn for different mass-mobility relations or charger configurations. The mass resolution of the mass distribution can be approximated by  $2\bar{m}/\Delta m$  where  $\Delta m$  is the full width of the transmitted mass distribution, and  $\bar{m}$  is the average transmitted mass. The additional factor of 2 included compared to Equation 4.10 is to account for  $\Delta m$  being the entire width of the distribution, not the half-width. As previously discussed, the resolution of a unipolar charger-PMA system is somewhat complicated owing to the multiple charge components arising due to the unipolar charger. Figure 4.8 demonstrates how the resolution of the transmitted mass distribution varies as a function of the average transmitted particle mass. Two cases are shown in Figure 4.8, one in which the scan profile is calculated for an  $R_{m,q} = 3$  (black circles) and

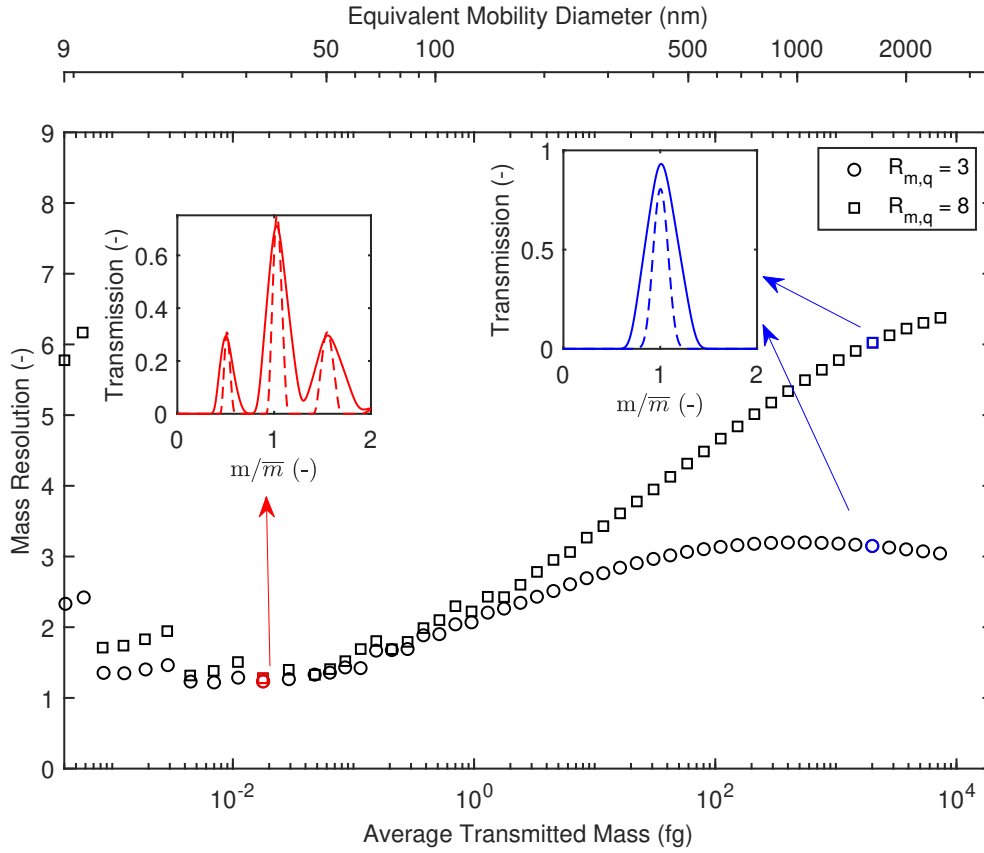


Fig. 4.8 Mass Resolution defined as,  $2\bar{m}/\Delta m$  as a function of the average particle mass, for two different resolutions,  $R_{m,q} = 3$  and  $R_{m,q} = 8$ . Note the additional factor of 2 included compared to Equation 4.10 is to account for  $\Delta m$  being the entire width of the distribution, not the half-width. The inset figures show the system transfer function for two example distributions, one for a smaller particle mass (red) where distinct charge states are visible and for a larger particle mass (blue) where charge states blur together. The solid line in each inset Figure is the distribution for  $R_{m,q} = 3$  and the dashed line for  $R_{m,q} = 8$ .

the other for an  $R_{m,q} = 8$  (black squares). For both cases, the resolution generally increases as the average transmitted mass of particles increases and, at larger masses, the resolution starts to plateau close to the intended operating resolution. At masses less than  $\sim 5$  fg (equivalent mobility size of the  $\sim 250$  nm), increasing the target resolution from 3 to 8 has minimal effect on increasing the resolution of the transmitted distribution. This is explained by the inset distribution shown in Figure 4.8. At smaller masses (given by the red distribution shown in the inset of Figure 4.8) the mass distributions are widely spread and distinguishable from one another owing to the greater degree of relative difference in the attainable charge states (*i.e.* smaller particles may attain charge states of 1, 2, 3.. which have a larger difference in relative terms compared to charge states of 20, 21, 22 for instance). The CPMA transfer function

dictates the distribution width at each integer charge state. Therefore, whilst increasing the resolution of the CPMA transfer function narrows the width of individual peaks (compare the dashed red line to the solid red line, which demonstrates distributions for  $R_{m,q} = 8$  and  $R_{m,q} = 3$ , respectively) it does not reduce the entire width of the distribution as this is dictated by the integer charge states present. The blue distribution shows a more narrowly distributed transmitted mass distribution at a larger size that reduces in width as the target resolution increases. Therefore, a unipolar charger-PMA system can select particles of a given average mass, but the distributed masses may have a significant spread, particularly when selecting smaller particles. It should also be noted that the experimental analysis in this work was only performed for particles less than 500 nm in size, if the INTAC method is to be used to determine the average transmitted mass for micron-sized particles, then, as previously discussed, a charging power law that incorporates field charging must be used; this could be obtained through a numerical model such as that of Lawless [101] or can be determined experimentally.

## 4.5 Conclusions

The INTAC algorithm enables rapid multiple charge correction in the CPMA without requiring additional measurement equipment. In this work, the INTAC algorithm is experimentally validated, and a new method is introduced for calculating the CPMA resolution profile for multiply charged particles. Through this approach, the CPMA's operating range is significantly extended while sufficient concentration and current signal are maintained for larger particles.

The INTAC technique was validated for three different  $n_{it}$  products using spherical particles, showing good agreement for particles smaller than 500 nm. Larger particles exhibited some field charging, which is not currently accounted for in the algorithm. However, as the average charge follows a predictable power-law relationship with particle size, the method is expected to extend to larger particles with further refinement.

The INTAC algorithm is reliable for spherical or compact aerosols with well-characterized mass-mobility relationships and charging performance. However, its application to non-spherical particles remains more uncertain due to additional uncertainties in the mass-mobility relationship and increased charging of agglomerates. Nevertheless, when both the mass-mobility and charge relations are measured for a given aerosol, the INTAC algorithm can estimate the average mass within approximately  $\pm 20\%$ . If higher accuracy is required, direct charge measurement using an electrometer and CPC remains the preferred method for multiple charge correction in unipolar charger-CPMA systems. However, this method

has two key limitations: (1) the additional flow required for an electrometer and CPC may compromise the CPMA's operating range at higher flow rates and may not be compatible with experimental setups, and (2) sufficient aerosol concentration is needed to generate a measurable electrometer signal. In these scenarios, the INTAC method is a serviceable alternative, although it is recommended that spherical aerosols are utilised to reduce errors.

Finally, numerical analysis indicates that using a unipolar charger and CPMA to select particles within a narrow mass range is feasible only at higher masses, where the charge distribution does not dominate the transmitted mass width. These findings provide key insights into the practical limitations and applications of charge correction in unipolar charger–CPMA systems, which is particularly useful for measurements of mass absorption cross-sections or for mass concentration calibrations using CERMS wherein a direct measure of average mass is not available.



## Chapter 5

# Experimental and Theoretical Validation of the Aerosol Mobility Separator Electrometer<sup>1</sup>

### 5.1 Introduction

It was discussed in Chapter 2 that measuring multiple particle metrics such as mass, aerodynamic diameter, or mobility diameter in tandem is a powerful tool for obtaining a better understanding of the structure of an aerosol. However, tandem classification in its present form can be time-consuming owing to the need to step/scan a downstream classifier across the width of the distribution produced by the upstream classifier. For example, the SMPS measurements for each CPMA set-point for the measurements in Chapter 4 took 2 - 3 min. Authors have made efforts to decrease measurement time, but they often suffer from several problems, including multiple charging artefacts, sensitivity to distribution width, and inadequate sizing resolution. To address some of these problems, this chapter introduces and validates a new aerosol classifier, the Mobility Separator Electrometer (MSE). The MSE is intended to be used downstream of existing classifiers to measure average particle electrical mobility. This is done using closed-loop control such that the classification voltage is automatically adjusted based on the ratio of the measured output of a pair of electrometers. This removes the need for stepping or scanning a downstream classifier, reducing the time required for typical tandem measurements. By measuring particle electrical mobility this device can be paired with a CPC downstream of either an AAC or CPMA for measurements of particle effective density. The operating principles are described and the theoretical

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transfer function of the MSE based on the work of Knutson and Whitby [98] is determined. The transfer function is then validated experimentally. A numerical model is implemented to probe tandem classification arrangements using the MSE for measurements of particle effective density. Experimental applications of the MSE in conjunction with an AAC are demonstrated to measure the effective density of DOS and Ammonium Sulphate. Finally, the limitations of the device are discussed.

## 5.2 The Mobility Separator Electrometer: Working Principle and Transfer Function

### 5.2.1 Working Principle

The basic principle of the MSE is similar to a zeroth-order mobility analyser or electrostatic precipitator described by Lehtimäki [104] and illustrated in Figure 5.1a. When an electric field is applied between two plates, charged particles experience an electrostatic force. More electrically mobile particles precipitate onto the walls whilst less mobile ones penetrate through the exit (indicated by the particle trajectories in Figure 5.1a). Lehtimäki [104] demonstrated that for a given applied voltage, the average particle electrical mobility can be determined from the current ratio between the precipitated and penetrating particles. In practice, a measurement of current within the femtoampere range in close proximity to an applied electric field is difficult because capacitive currents induced by a changing electric field can easily exceed the genuine signal. To circumvent this problem, in the MSE, a clean sheath flow is provided to collect the higher mobility particles towards a second external detector.

Figure 5.1b shows a schematic of the MSE. Particle-laden air flows through the inlet labelled sample flow, and HEPA-filtered air enters the sheath flow inlet in a concentric arrangement. A voltage is applied between the outer and inner cylinder such that charged particles experience an electrostatic and drag force in the radial direction. In this regard, the MSE classifies particles by their charge-to-drag ratio, which is commonly referred to as electrical mobility,  $Z_p$ . Particle electrical mobility is defined as [70]

$$Z_p = qeB = \frac{qeC_c}{3\pi\mu d_m} \quad (5.01)$$

where  $q$  is the number of elementary charges on the particle,  $e$  is the charge of an electron, and  $B$  is the particle's mechanical mobility. The mechanical mobility can be related to the particle mobility diameter,  $d_m$  through  $C_c$ , the Cunningham Slip Correction factor and  $\mu$ ,

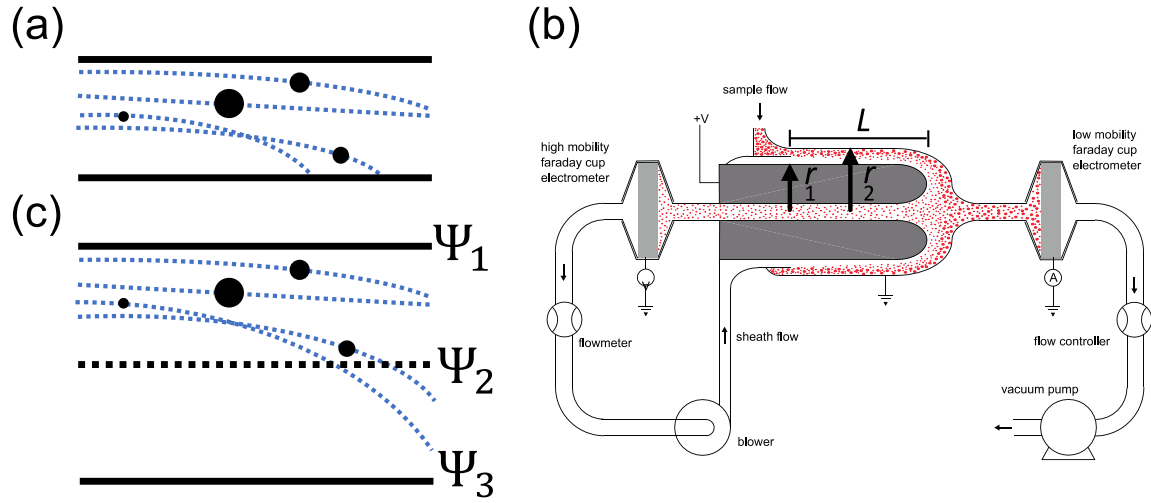


Fig. 5.1 Schematic diagrams of (a) a zeroth-order mobility analyser or electrostatic precipitator with example particle trajectories, (b) the MSE including hardware and labels of the various components within the device, (c) fluid streamlines within the MSE classification region with example particle trajectories, where  $\Psi_1$   $\Psi_3$  correspond to the outer and inner radii of the classification region and  $\Psi_2$  represents the splitting streamline between the sample and sheath flows.

the air viscosity. Within this work, the empirical relations of air viscosity and Cunningham slip correction determined by Kim et al. [95] are used. Particles of low electrical mobility follow the sample flow stream (to the right on the diagram), whereas more electrically mobile particles can migrate from the sample flow into the recirculating sheath flow (to the left) under the action of the electric field. It should be noted that once particles move towards the high mobility exit, they experience no further electrostatic force and only follow the flow streamlines. The charged particles within the sample and sheath flows are collected on two separate filters inside a shielded Faraday cup, referred to as the low- and high-mobility Faraday cup electrometer (FCE), respectively. The current induced by the charged particles is determined by means of an electrometer circuit. In its present mode of operation, the flow rate through the low mobility FCE and high mobility FCE are designed to equal the sample flow and sheath flow rates, respectively. The inner and outer radii of the MSE are 7 mm and 8.75 mm respectively and the geometric length of the classification region is 46.03 mm.

The use of a voltage and sheath flow to classify particles by their electrical mobility is the same principle as a conventional DMA. However, there are several key distinctions between the two classifiers. Firstly, the MSE is operated at a low sheath-to-sample flow ratio (this is commonly referred to as resolution when discussing DMAs) to achieve the desired flow ratio range between the electrical mobility at which all particles pass to the low mobility outlet and that for which all pass to the high mobility outlet. The balance allows the MSE to measure all

particles. Secondly, the MSE is optimised for use with unipolarly charged particles rather than bipolarly charged particles. Unipolarly charging an aerosol increases the number of chargers per particle, which has the effect of increasing particle electrical mobility whilst reducing the variance in the distribution of mobilities[18]. Therefore, the MSE needs only to classify a much smaller range of electrical mobilities ( $\sim 1 \times 10^{-6} \text{ m V}^{-2} \text{ s}^{-1}$  to  $1 \times 10^{-8} \text{ m V}^{-2} \text{ s}^{-1}$ ) relative to a conventional DMA ( $\sim 1 \times 10^{-6} \text{ m V}^{-2} \text{ s}^{-1}$  to  $1 \times 10^{-9} \text{ m V}^{-2} \text{ s}^{-1}$ ). Note that this range of electrical mobilities for the MSE equates to an operating range in mobility diameter of 10 nm to 5000 nm when the particles are unipolarly charged but only a maximum classification diameter of 150 nm when measuring singly charged particles. The final and main difference between a DMA and an MSE is that the ratio of the currents in the low mobility to high mobility electrometers in the MSE gives an instantaneous indication of electrical mobility, unlike a conventional DMA in which the voltage must be scanned to identify the particle size. In the MSE, the classification voltage is closed-loop controlled to maintain the ratio of the two integral mobility streams to equal values, which, as will be shown in the following section, is the criterion for measuring the average electrical mobility of the sampled aerosol population.

### 5.2.2 Theoretical Transfer Function: Non-Diffusing Particle Streamline Model

The following analysis is strictly for the straight portion of the classifier (*i.e.* up to the geometric length,  $L$ , indicated in Figure 5.1b). The classification section necessarily curves at the end to split the flow between the two external detectors. This will likely affect the flow and the classification of the particles. As will be shown experimentally, the length of the classifier can be well approximated by an effective length. More complete computational approaches that consider finite element simulations of the fluid flow and electric field in the full geometry of the classifier could be considered in the future to obtain a more accurate determination of the transfer function [116].

The trajectory of a non-diffusing particle with electrical mobility  $Z_p$ , within the outside annulus of the MSE, operating with a voltage  $V$  is given by the following equations:

$$\frac{dr}{dt} = \frac{VZ_p}{r \ln\left(\frac{r_2}{r_1}\right)} \quad (5.02)$$

$$\frac{dx}{dt} = u_x(r) \quad (5.03)$$

where  $r$  and  $x$  are the radial and axial coordinates,  $t$  is time and  $u_x$  is the component of flow in the axial direction. It is assumed that the flow velocity only has a component in the radial direction. Knutson and Whitby [98] proposed a mathematical model using a stream function  $\Psi$  and electric flux function  $\Phi$  to determine the well-known DMA transfer function. These are given by:

$$\Psi(r, x) = \int ru_r dx - ru_x dr \quad (5.04)$$

and

$$\Phi(r, x) = \int rE_r dx - rE_x dr. \quad (5.05)$$

The same authors demonstrated that particles that move along specific non-diffusing trajectories satisfy the constraint

$$\Delta\Psi + Z_p\Delta\Phi = 0. \quad (5.06)$$

Under this model, all particles that traverse the DMA begin and end at the same values of  $\Phi_{\text{in}}$  and  $\Phi_{\text{out}}$ , as the electric field must disappear within the inlet and exit such that  $\Delta\Phi$  is the same for all particles. This argument can be made in the same vein for the MSE. The above equation can then be rearranged by considering a pair of inlet,  $\Psi_{\text{in}}$ , and exit streamlines  $\Psi_{\text{out}}$ , such that

$$\Psi_{\text{out}} = \Psi_{\text{in}} - Z_p\Delta\Phi \quad (5.07)$$

The transfer functions of the two outlets of the system are defined by the following equations [188];

$$\Omega_L = \int_{\Psi_1}^{\Psi_2} \left[ \int_{\Psi_1}^{\Psi_2} f_{\text{trans}}(\Psi_{\text{out}}, \Psi_{\text{in}}) d\Psi_{\text{out}} \right] f_{\text{in}}(\Psi_{\text{in}}) d\Psi_{\text{in}} \quad (5.08)$$

$$\Omega_H = \int_{\Psi_1}^{\Psi_2} \left[ \int_{\Psi_2}^{\Psi_3} f_{\text{trans}}(\Psi_{\text{out}}, \Psi_{\text{in}}) d\Psi_{\text{out}} \right] f_{\text{in}}(\Psi_{\text{in}}) d\Psi_{\text{in}} \quad (5.09)$$

where  $\Omega_L$  and  $\Omega_H$  represent the transfer function of the low-mobility and high-mobility outlets, respectively. The differential element  $f_{\text{in}}(\Psi_{\text{in}}) d\Psi_{\text{in}}$  is the probability of particle entering the classifier on a streamline between  $\Psi_{\text{in}}$  and  $\Psi_{\text{in}} + d\Psi_{\text{in}}$  and  $f_{\text{trans}}(\Psi_{\text{out}}, \Psi_{\text{in}}) d\Psi_{\text{out}}$  is the probability that a particle entering on a streamline  $\Psi_{\text{in}}$  exits on a streamline between  $\Psi_{\text{out}}$  and  $\Psi_{\text{out}} + d\Psi_{\text{out}}$ . The three critical streamlines of the MSE are  $\Psi_1$ ,  $\Psi_2$  and  $\Psi_3$  are shown in Figure 5.1c.  $\Psi_3$  and  $\Psi_1$  bound the total flow in the classifier and describe the streamlines of the inner and outer radii of the classifier, respectively.  $\Psi_2$  is the streamline that separates the sample flow from the sheath flow.

It is assumed that there is equal probability that a particle enters on an inlet streamline between  $\Psi_1$  and  $\Psi_2$  at the aerosol inlet such that  $f_{\text{in}}$  takes the form of a uniform probability

density function,

$$f_{\text{in}}(\Psi_{\text{in}}) = \frac{1}{\Psi_2 - \Psi_1}. \quad (5.10)$$

For a particle entering on an aerosol inlet streamline  $\Psi_{\text{in}}$ , the probability density function given that it exits on a streamline  $\Psi_{\text{out}}$  can be written as

$$f_{\text{trans}}(\Psi_{\text{out}}, \Psi_{\text{in}}) = \delta_D(\Psi_{\text{out}} - \Psi_{\text{in}} + Z_p \Delta \Phi) \quad (5.11)$$

where  $\delta_D$  is the Dirac delta function. Equations 5.10 and 5.11 can be substituted directly into Equations 5.08 and 5.09 and solved analytically. The transfer functions of the low and high-mobility particle outlets take the following forms

$$\Omega_L = \frac{1}{2} \left[ - \left| \frac{Z_p}{\bar{Z}_p} \right| + \left| 1 + \frac{Z_p}{2\bar{Z}_p} \right| + \left| 1 - \frac{Z_p}{2\bar{Z}_p} \right| \right] \quad (5.12)$$

$$\Omega_H = \frac{1}{2} \left[ \left| \frac{Z_p}{2\bar{Z}_p} \right| + \left| 1 + \frac{1}{\beta} - \frac{Z_p}{2\bar{Z}_p} \right| - \left| 1 - \frac{Z_p}{2\bar{Z}_p} \right| - \left| \frac{1}{\beta} - \frac{Z_p}{2\bar{Z}_p} \right| \right] \quad (5.13)$$

where  $\beta$  is the ratio of aerosol to sheath flow rate. The average mobility of a particle that enters on the midway streamline of the aerosol inlet flow (*i.e.*, between  $\Psi_1$  and  $\Psi_2$ ) and exits on the streamline that defines the boundary between the aerosol and sheath flow (*i.e.*,  $\Psi_2$ ) is given as

$$\bar{Z}_p = - \frac{Q_a \ln(r_2/r_1)}{4\pi V L}. \quad (5.14)$$

where  $Q_a$  is the sample flow rate (which is equal to the flow rate through the low mobility electrometer),  $r_2$  and  $r_1$  are the outer and inner radii of the MSE,  $V$  is the applied voltage, and  $L$  the classifier length. The low mobility transfer function is independent of the sheath flow rate, as whether a particle migrates across the bounding streamline between the sample and sheath flow is only a function of the electrical mobility of the particle, the sampling flow rate and the applied voltage. Meanwhile, the high mobility transfer function depends on the sheath flow rate. However, the linear portion of the transfer function for both outlets is independent of the sheath flow rate as the high mobility transfer function must necessarily balance the low mobility transfer function. An example of the non-diffusing transfer function of the MSE is shown in Fig. 5.2. Also indicated in the figure is the penetration through the device (black dashed line) as a function of electrical mobility. The value of the penetration remains equal to unity until the end of the flat top section of the high mobility outlet, thus allowing complete measurement of the charged particle current by summing the currents measured by the high and low mobility electrometers. Furthermore, the average mobility, given by Equation 5.14, is determined by balancing the electrometer currents between the

high and low mobility outlets (*i.e.*,  $\Omega_H = \Omega_L = 0.5$ ). In this regard, closed-loop control can be utilised to alter the voltage such that this criterion is maintained without any user input.

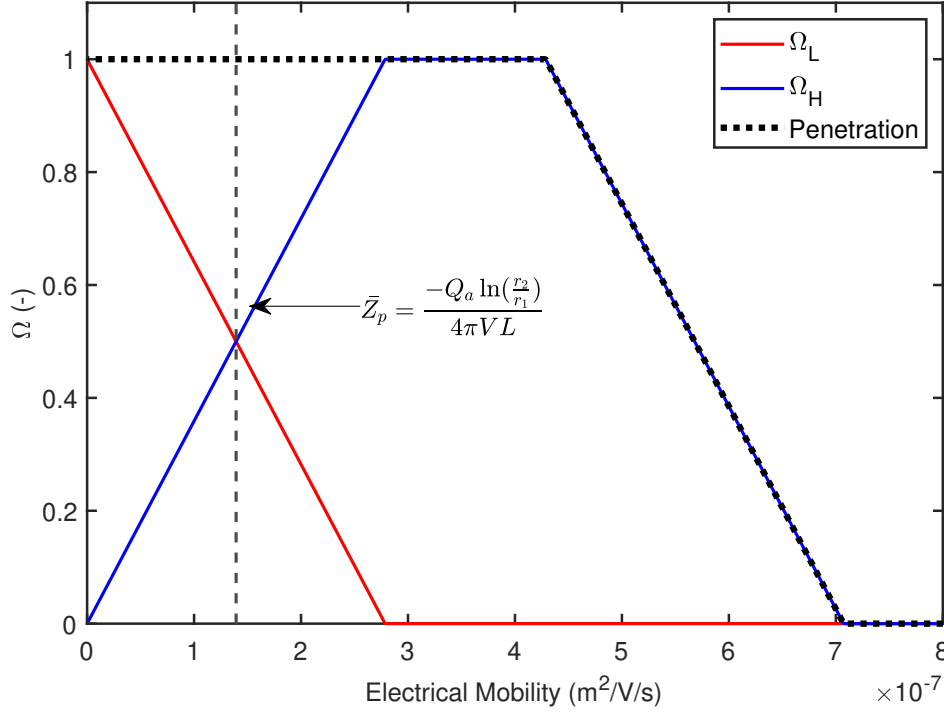


Fig. 5.2 Analytical representation of the MSE non-diffusing transfer function given by Equations 5.12 and 5.13. The transfer function was calculated for an operating voltage of  $-30$  V and aerosol and sheath flow rates of  $Q_a = 0.65 \text{ L min}^{-1}$  and  $Q_{sh} = 1 \text{ L min}^{-1}$ . The length and outer and inner radii of the classifier were taken to be  $46.03$  mm,  $8.75$  mm and  $7$  mm, respectively.

A final note is required on the linearity of the MSE transfer function. The MSE has been designed to be operated in the region of the transfer functions where both the high and low mobility functions are linear (see left-hand side of Fig. 5.2). In this case, the transfer functions take the simplified form of

$$\Omega_L = 1 - \frac{Z_p}{2\bar{Z}_p} \quad \text{for } Z_p \leq 2\bar{Z}_p \quad (5.15)$$

$$\Omega_H = \frac{Z_p}{2\bar{Z}_p} \quad \text{for } Z_p \leq 2\bar{Z}_p. \quad (5.16)$$

As the MSE operates with closed-loop control, there may be conditions where the balance between the two electrometers may see small deviations. However, since the transfer function

is linear, the voltage that provides balanced outputs can be easily determined using either Equation 5.15 or 5.16.

## 5.3 Tandem Measurements with the MSE

Owing to its broad transfer function, the MSE does not work as a stand-alone classifier equivalently to a conventional DMA. Operating the MSE in the overlapping linear region of the transfer function requires distributions that are neither broad nor heavily skewed, as these would make the assumptions around the point of equal current difficult to interpret. The intended use of the MSE is, therefore, more niche and best combined with prior classification. A typical expected experimental set-up incorporating the MSE is shown in Figure 5.3. Particles are first charged using a unipolar diffusion charger, in which many charges are acquired per particle. Particles can be classified using either an AAC or CPMA, which classify an aerosol by particle relaxation time and mass-to-charge ratio, respectively [145, 194]. The classified distribution is then sampled in parallel by a CPC and the MSE. In this regard, the experimental set-up is extremely similar to conventional distribution measurements wherein the number concentration is measured downstream of a classifier to measure a particle size distribution. However, the addition of the MSE allows for further aerosol characterisation through the additional measurement of the average charge and mobility diameter, which is inaccessible with just a single classifier and CPC. This enables the characterisation of size-dependent particle density, which indicates particle structure. The calculation methods used to determine effective density using the experimental set-up in Figure 5.3 are described in detail in the following section.

### 5.3.1 Calculating Particle Effective Density

The particle effective density can be calculated in a similar manner to that described in Section 2.3.1. However, for clarity and ease of reading, some of the relevant steps are also included here to avoid the need for cross-referencing. Additionally, slight modifications are required in the calculation of particle mass and mobility diameter due to the presence of multiply charged particles.

Particle effective density is defined as the ratio of particle mass  $m$  to that of a mobility-equivalent particle volume,  $V_m = \pi d_m^3/6$ , so that the effective density is given by

$$\rho_{\text{eff}} = \frac{6m}{\pi d_m^3}. \quad (5.17)$$

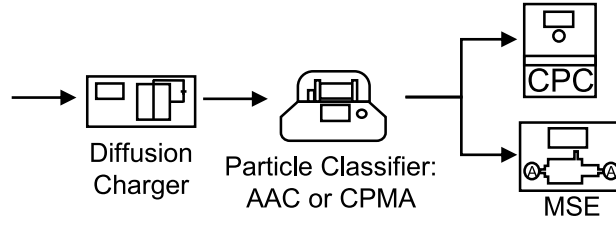


Fig. 5.3 Typical tandem measurement setup applicable to measurements with the MSE and pre-existing aerosol instrumentation. This experimental set-up consists of a unipolar diffusion charger and particle classifier followed by parallel sampling between a CPC and MSE.

Note there are other definitions of effective density, which are summarised by DeCarlo et al. [42]. Therefore, measurements of mass and  $d_m$  can be used directly to calculate the effective density. The product of particle mass and particle mechanical mobility ( $B = \frac{C_c(d_m)}{3\pi\mu d_m}$ ) is referred to as the particle relaxation time,

$$\tau = mB = \frac{\rho_{\text{eff}} C_c(d_m) d_m^2}{18\mu}. \quad (5.18)$$

The particle relaxation time can be expressed in terms of aerodynamic diameter,  $d_a$ , which is defined as a spherical particle with unit density ( $\rho_0 = 1000 \text{ kg m}^{-3}$ ) which has the same terminal settling velocity as the particle of interest,

$$\tau = \frac{\rho_0 C_c(d_a) d_a^2}{18\mu}. \quad (5.19)$$

Equating Equations 5.18 and 5.19 provides the following equation for the calculation of effective density from parallel measurements of aerodynamic and mobility diameters.

$$\rho_{\text{eff}} = \rho_0 \frac{d_a^2 C_c(d_a)}{d_m^2 C_c(d_m)}. \quad (5.20)$$

Pairwise measurements of  $m$  and  $d_m$  or  $d_a$  and  $d_m$  can be obtained by the classification of particles with a CPMA or AAC before parallel measurement with a CPC and the MSE, respectively. The classifier set-points of the CPMA and AAC can be used to calculate the average mass and aerodynamic diameter transmitted through the classifier. It is therefore assumed that the average of the downstream particle property distribution (mass or aerodynamic diameter) is not skewed in any manner such that the classifier centroid values can be used to approximate the quantity of interest without concern for the overall particle size and charge distribution. The AAC uses the balance of drag and centrifugal forces on the particles and classifies them based on their relaxation time. The particle relaxation time can

be determined from the operating conditions of the AAC<sup>2</sup> by [194]

$$\tau^* = \frac{2Q_{sh}}{\pi\omega^2(r_1 + r_2)^2L} \quad (5.21)$$

where  $\tau^*$  is the nominal relaxation set-point of the AAC,  $Q_{sh}$  is the sheath flow rate,  $\omega$  the classifier rotational speed,  $r_1$  and  $r_2$  are the inner and outer classifier radii and  $L$  is the length of the classifier. Aerodynamic diameter can then be calculated from the relaxation time set-point by iteratively solving Equation 5.19.

Unlike the AAC, the CPMA is charge-dependent as it classifies particles based on their mass-to-charge ratio, which is given by

$$s^* = \frac{m}{q} = \frac{eV}{\omega_c^2 r_c^2 \ln(\frac{r_2}{r_1})}, \quad (5.22)$$

where  $s^*$  is the nominal mass-to-charge setpoint of the CPMA,  $V$  and  $\omega_c$  are the voltage and average rotational speed applied to the CPMA classifier and  $r_2$ , and  $r_1$  are the radii of the outer and inner cylinder, respectively.  $r_c$  is the average of the inner and outer radii.  $e$  is the charge on an electron, and  $q$  is the number of elementary charges held by the particle. The charge on the aerosol is required to determine the average mass. The average charge on a population of particles can be determined by a combination of an electrometer and CPC and is given by

$$\bar{q} = \frac{i}{kNQ_a e} \quad (5.23)$$

where  $i$  is the electrometer current,  $Q_a$  is the electrometer flow rate,  $N$  is the number concentration measured by the CPC, and  $k$  is a calibration factor to account for differences between the electrometer and CPC counting efficiencies. Therefore, by sampling in parallel with a combination of a CPC and the MSE, the average particle charge can be measured, since the total current can be determined by the sum of the currents of the low and high-mobility electrometer outlets. The average transmitted particle mass downstream of the CPMA can then be determined by combining Equations 6.13 and 6.14. The approximation of the average transmitted mass as

$$\bar{m} \approx s^* \bar{q}, \quad (5.24)$$

is based on the assumption that the average charge corresponds to particles of mass  $\bar{m}$ . Therefore, the mass distribution downstream of the classifier is assumed not to be skewed due to the width of the particle charge distribution, CPMA transfer function or input size distribution.

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<sup>2</sup>For an AAC that is operated with balanced flows.

The MSE provides a measure of average electrical mobility as given by Equation 5.14 by balancing the high and low electrometer currents. To calculate mobility diameter from electrical mobility using Equation 6.17, the charge on the particle is required. To determine the average particle mobility diameter, it is assumed that the average charge determined by Equation 6.14 and the average electrical mobility by Equation 5.14 correspond to the average particle mobility diameter,  $\overline{d_m}$  of the sampled population of particles. Again, this assumes that the quantities of charge, electrical mobility and mobility diameter are narrowly distributed and not skewed such that average quantities can be used in the following equation

$$\overline{Z_p} = \frac{\overline{q}eC_c(\overline{d_m})}{3\pi\mu\overline{d_m}} \quad (5.25)$$

to determine the average particle mobility diameter downstream of either the AAC or CPMA. Using the combined measurements of mass and mobility diameter (Equations 5.24 and 5.25) or aerodynamic diameter and mobility diameter (Equations 5.19 and 5.25), Equations 6.18 and 5.20 can be used to determine average the effective density with either a CPMA or AAC classification system, respectively. A numerical model can be used to evaluate the extent to which the assumption of narrowly distributed particle properties after classification is valid and, therefore, whether this method of determining the effective density is accurate. The numerical model used is discussed in the following section.

## 5.4 Numerical Model of the Tandem Classification System

In the previous section, the methodology for determining the effective density from the measurements of a unipolar charger-classifier-MSE-CPC system was described. It was assumed that the average measured quantities could be used to determine the effective density as a function of the classifier set-point without regard for the underlying distributions. In reality, there is a distribution of particle properties such as charge, mobility, diameter and mass downstream of the classifier, which is dependent on a number of factors, including the sampled particle distribution and the effective density relation, classifier transfer functions and the particle charge distribution as a function of particle size. It is therefore important to understand how the estimation of the particle effective density detailed in section 5.3.1, which only utilises average quantities, compares to the true size-dependent effective density of the sampled aerosol. Furthermore, experimental parameters may vary between set-ups and understanding best practices when combining existing and new instrumentation is paramount in achieving accurate measurements. A numerical model allows for examination of the methodology of determining effective density for different aerosols with varying effective

density relations, as well as investigation of the effect of different experimental conditions such as  $n_{it}$  product, classifier resolution and particle size distribution width.

To investigate the validity of the proposed method for determining particle effective density, the convolution of the components of the set-up depicted in Figure 5.3 have been numerically modelled. This model enables simulation of the response of the experimental set-up for a known particle size distribution and effective density relation. The response of the MSE to a classified aerosol can be simulated, which, in conjunction with the modelled classifier set-point, can be used to determine the effective density. This determined effective density can then be directly compared to the model input effective density to determine the accuracy of the method. This numerical model is similar to those of Sipkens et al. [180] and Johnson et al. [84] who both combined models of a unipolar charger and the CPMA. Sipkens et al. [180] demonstrated methods for rapid computation of the average transmitted particle mass through a unipolar charger-particle mass analyser system through a series of average charge algorithms. This approach allows for the prediction of the average mass transmitted by such systems, accounting for multiple charging, when additional downstream measurements are not feasible. Johnson et al. [84] also included a model of the DMS500 downstream of the CPMA, which was used to determine the effective density of several different types of aerosol particles [84, 82, 83]. Herein, the differential mobility analyser model used in Johnson's work is replaced with a model of the MSE and CPC. Furthermore, the addition of an AAC, instead of a CPMA, is included to demonstrate the applicability of measuring particle effective density using an aerodynamic as well as a mass-based classification method.

#### 5.4.1 Evaluating the calculation of effective density using a numerical model

To determine the particle effective density, as described in Section 5.3.1, the classifier set-point —  $\tau^*$  or  $s^*$  for the AAC and CPMA respectively — the average particle charge downstream of the classifier, and the average particle electrical mobility determined from the MSE are required. Firstly, a demonstration that classifier set-points, given by Equations 5.21 and 5.24, are equivalent to the average of the downstream population of the quantity of interest is warranted. The number-weighted average of some property  $x$  measured downstream of a unipolar charger followed by a classifier is

$$\bar{x} = \frac{\int \sum_{q=1}^{\infty} x f_q(x) \Lambda(x) n(x) dx}{\int \sum_{q=1}^{\infty} f_q(x) \Lambda(x) n(x) dx} \quad (5.26)$$

where  $x$  is the particle property of interest, such as mass, aerodynamic diameter or mobility diameter.  $f_q(x)$  is the fraction of particles with  $q$  elemental charges,  $\Lambda(x)$  is the transfer function of the upstream classifier and  $n(x)$  is the upstream particle distribution as a function of the property  $x$ . Comparison of the classifier set-points given by Equations 5.21 and 5.24 to the corresponding average quantity downstream of the classifier calculated using Equation 5.26 can be used to determine the applicability of classifier centroid values to describe the mean of the downstream aerosol population. Note that here, the average is calculated only for particles carrying charge. Neutral particles can penetrate either the AAC or CPMA classifier depending on the operating conditions of the classifier, particle size and particle charge distribution. However, since the calculation of particle effective density requires particles to be charged, only particles carrying at least one charge are considered.

After classification by either the AAC or CPMA, the aerosol is sampled in parallel by the MSE and a CPC. To simulate the response of the MSE, the voltage  $V^*$  that ensures that the current is split equally between the high and low mobility outlet needs to be determined. The current measured by the low-mobility electrometer can be calculated from

$$i_L = eQ_a \int \sum_{q=1}^{\infty} q f_q(x) \Lambda(x) \Omega_{\text{MSE,L}}(V^*, Z_p) n(x) dx \quad (5.27)$$

and similarly for the high-mobility electrometer

$$i_H = eQ_a \int \sum_{q=1}^{\infty} q f_q(x) \Lambda(x) \Omega_{\text{MSE,H}}(V^*, Z_p) n(x) dx. \quad (5.28)$$

The high and low transfer functions of the MSE were modelled using the theoretical model given by Equations 5.12 and 5.13, respectively. A root finder (Python's/MATLAB's fsolve package) was used to determine the classifier voltage,  $V^*$ , which satisfied the matching condition for the MSE, namely,  $i_H = i_L$  as a function of electrical mobility. The value of  $V^*$  was then substituted into Equation 5.14 to determine the average particle electrical mobility. To mimic experimental scenarios, the model is only evaluated at points at which the total current measured by the MSE is greater than 10 fA.

The average charge is required to determine the average transmitted mass using Equation 5.24 and the average mobility diameter through Equation 5.25. The average charge, as measured by the combination of the MSE and CPC, is given by

$$\bar{q} = \frac{i_H + i_L}{Q_a e N_{\text{CPC}}}, \quad (5.29)$$

where  $N_{\text{CPC}}$  is the concentration measured by the CPC which is given by

$$N_{\text{CPC}} = \int \sum_{q=0}^{\infty} \eta(x) f_q(x) \Lambda(x) n(x) dx. \quad (5.30)$$

where  $\eta(x)$  is the size-dependent counting efficiency of the CPC. The counting efficiency of the CPC was assumed to be unity and, therefore, not diameter-dependent within this work. This approximation is reasonable between 10 nm and  $\sim 1 \mu\text{m}$  for most ultrafine condensation particle counters. However, the upper limit of detection for CPCs depends on geometric details, as inertial losses occur which can reduce the counting efficiency at larger sizes. For instance, Tran et al. [201] and Sang-Nourpour and Olfert [168] respectively showed that the counting efficiencies of a TSI 3775 and a TSI 3776 CPC were reduced at sizes larger than  $1.5 \mu\text{m}$  aerodynamic diameter. A reduction in CPC counting efficiency would reduce the average charge compared to its correct value, resulting in underestimations in both the particle mass and particle mobility diameter. Note that, unlike the electrometer measurements, the summation over all charge states starts from  $q = 0$ , showing that CPCs count neutral particles whereas electrometers do not. This is an important distinction to make, as average charge measurements will be biased by the presence of neutral particles.

To evaluate the numerical model, a test aerosol is required, which can be defined by a distribution function and effective density relation, formulations of the transfer functions of the AAC and CPMA, and a model for the particle charge distribution as a function of particle size. The formulations of these are described below.

## 5.4.2 Aerosol Size Distribution and Density Relation

### Single-valued Mass mobility relation

Here, the model assumes that each test aerosol follows a mono-modal lognormal mobility diameter distribution,  $n(d_m) = dn/d\log d_m$ , which can be described by the total number,  $N$ , count median diameter ( $d_g$ ) and geometric standard deviation ( $\sigma_g$ ). To determine the distribution in a different property space (e.g., mobility diameter vs aerodynamic diameter), a model of the effective density of the particle is required. Here, it is assumed that the particle effective density can be described by an empirical power law relationship [128]

$$\rho_{\text{eff}} = k d_m^{(D_m-3)}, \quad (5.31)$$

which is also commonly phrased in terms of the effective density of a 100 nm mobility-sized particle,  $\rho_{100}$  as

$$\rho_{\text{eff}} = \rho_{\text{eff},100} \left( \frac{d_m}{100} \right)^{(D_m-3)}, \quad (5.32)$$

to provide an anchoring point for the relationship. Four commonly used aerosols have been investigated; DOS (Dioctyl Sebacate,  $k = 913$ ,  $\rho_{\text{eff},100} = 913 \text{ kg m}^{-3}$ ,  $D_m = 3$ ) and Ammonium Sulphate ( $k = 1770$ ,  $\rho_{\text{eff},100} = 1770 \text{ kg m}^{-3}$ ,  $D_m = 3$ ) which has been assumed to produce spherical particles of the same density as the material density, Sodium Chloride ( $k = 657.4$ ,  $\rho_{\text{eff},100} = 1905 \text{ kg m}^{-3}$ ,  $D_m = 2.934$ ), which produces cubic particles [155, 229] and Soot, which produces particles following the experimentally fit universal soot relation [147] ( $k = 0.1168$ ,  $\rho_{\text{eff},100} = 510 \text{ kg m}^{-3}$ ,  $D_m = 2.48$ ). The count median diameters for each aerosol were chosen as follows: 300 nm, 100 nm, 100 nm, 150 nm based approximately on Scanning Mobility Particle Sizer (SMPS) measurements of each aerosol, respectively. For all aerosols, the total number concentration was taken as  $1 \times 10^6 \text{ cm}^{-3}$  with a geometric standard deviation of 1.8. A parametric variation study also evaluated the effect of geometric standard deviation.

### Two-dimensional Mass Mobility Distributions

The previous description of an aerosol assumes that the mass-mobility relation is single-valued (*i.e.*, at a given mobility diameter, there is only a single value of mass that the aerosol can take). This assumption is aerosol-dependent and not strictly true for agglomerate aerosols such as soot. For soot, there is a distribution of masses at each mobility diameter owing to the variety of morphologies existing at each size [202, 183, 161, 22]. To address this, a two-dimensional distribution must be formulated, enabling a covarying relationship between mass and mobility. The two-dimensional mass-mobility distribution can be represented in a number of ways. Initial analysis by Buckley et al. [22] considered a two-dimensional mass-mobility distribution with a lognormal distribution in mobility space and a conditional mass distribution represented by a normal distribution. Here, a two-dimensional distribution is considered as proposed by Sipkens et al. [181], which assumes that the mobility diameter distribution can be described as lognormal and the conditional mass distribution, that is, the distribution of masses at a given mobility diameter also follows a lognormal distribution such that the two-dimensional mass mobility distribution takes the form

$$\frac{\partial^2 n}{\partial \log d_m \partial \log m} = \frac{N_{\text{tot}}}{2\pi \log \sigma_{d_m} \log \sigma_{m|d_m}} \exp \left( \frac{-(\log d_m - \log d_g)^2}{2 \log^2 \sigma_{d_m}} - \frac{(\log m - \log m_g|d_m)^2}{2 \log^2 \sigma_{m|d_m}} \right). \quad (5.33)$$

$\sigma_{d_m}$  is the standard deviation of the marginal mobility distribution,  $d_g$  is the count median diameter and  $N_{\text{tot}}$  is the total aerosol concentration. These values are taken to be equal to 1.8, 150 nm and  $1 \times 10^6 \text{ cm}^{-3}$ , respectively, to match the analysis of the one-dimensional distribution of a representative soot aerosol.  $\sigma_{m|d_m}$  is the geometric standard deviation of the mass distribution conditional on a given mobility diameter.  $\sigma_{m|d_m}$  is assumed to be independent of particle mobility diameter (*i.e.*, taken as a constant parameter). The geometric mean mass at a given mobility diameter,  $m_g|d_m$ , can be calculated from the effective density relation as follows given by Equation 5.31

$$m_g|d_m = \frac{\pi}{6} \rho_{\text{eff}} d_m^3 = \frac{\pi}{6} k d_m^{D_m}. \quad (5.34)$$

Therefore, the distribution in log-log mass-mobility space is centred around a line of gradient  $D_m$ , with the geometric standard deviation of the conditional mass distribution dictating the spread.  $k$  and  $D_m$  are taken as equal to  $0.1168 \text{ kg m}^{-2.48}$  and 2.48, respectively, as in the case where it was assumed that the mass-mobility relation is single-valued. The analysis proceeds identically as the single-valued case but noting that the analysis is now performed on a two-dimensional grid, with equally spaced points in logarithmic space in both mass and mobility. The conditional mass width was varied from 1.05, indicating narrowly distributed aerosols, to 1.5, describing a broad array of particle morphologies. The analysis for the two-dimensional case was performed using code edited from the work of Sipkens et al. [181].

### 5.4.3 Particle Charging

In unipolar diffusion charging, a high flux of ions is generated from a unipolar source such as corona discharge to transfer charge to particles. The most commonly used model for unipolar charging is that proposed by Fuchs [49]. This model provides a method to determine the charge distribution on a particle for a given diameter by applying a limiting sphere method to determine the ion-aerosol attachment rate. More recent models have employed Langevin Dynamics Simulations, which allow for a more robust determination of the collision kernel for particles of an arbitrary shape [107]. These models provide better estimations of the

attachment coefficients for a wide range of aerosols with differing morphological properties but are computationally expensive to run. The limiting sphere model of Fuchs [49] also neglects the effect of external electrical fields within the charger. This is generally not a problem for particles less than 1  $\mu\text{m}$ ; however, field charging becomes the dominant mode of charging above this size. As both the CPMA and AAC have size limits up to 5  $\mu\text{m}$ , field charging is potentially an important charging mechanism. However, numerical experiments showed minimal difference in the resulting analysis when using the model of Lawless [101], which includes an electric field charging term with an electric field strength matching that in the commercial Cambustion Unipolar Diffusion Aerosol Charger. The comparison between Fuchs' and Lawless' models is detailed in the Appendix C. The present analysis reverts to the original Fuchs' model.

The charge distribution on a particle,  $f_q(d_m, n_i t, \epsilon)$ , is considered to be a function of the ion concentration-time product,  $n_i t$ , the particle mobility diameter and the particle conductivity,  $\epsilon$ , for a given set of gas conditions. The charge distribution was calculated at a temperature and pressure of 293 K and 101 325 Pa for air, with ionic molecular weight and mobility of 0.109 kg mol<sup>-1</sup> and 1.4 cm<sup>2</sup> V<sup>-1</sup> s respectively [158]. The initial value of the  $n_i t$  product is assumed as  $1 \times 10^{14}$  s m<sup>-3</sup>, but the the potential effects of a range of values of  $n_i t$  is also analysed.

#### 5.4.4 Classifier Transfer Functions

##### AAC

To determine the distribution of particles downstream of each classifier, the transfer function is required, which describes the probability that a particle of a given size will exit the classifier for a given set of operating conditions. The experimentally parameterised transfer function of the AAC operating with balanced flows, as measured by Johnson et al. [79], has been used.

$$\Lambda_{\text{AAC}} = \frac{\lambda_{\Lambda} \mu_{\Lambda}^2}{2\beta} \left[ \left| \tilde{\tau} - \left( 1 + \frac{\beta}{\mu_{\Lambda}} \right) \right| + \left| \tilde{\tau} - \left( 1 - \frac{\beta}{\mu_{\Lambda}} \right) \right| - 2|\tilde{\tau} - 1| \right] \quad (5.35)$$

where  $\beta = \frac{Q_a}{Q_{sh}}$  and  $\tilde{\tau} = \frac{\tau}{\tau^*}$  are the inverse resolution and non-dimensional relaxation time, respectively.  $\tau^*$  is the nominal relaxation time given by Equation 5.21. Equation 5.35 includes two scaling parameters relative to the theoretical transfer function [194],  $\lambda_{\Lambda}$  and  $\mu_{\Lambda}$ , which independently alter the integrated area and width of the transfer function, respectively. Johnson et al. [79] found that the loss factor of the AAC increased from 0.44 to 0.8 as particle size increased, and the broadening factor increased from 0.4 to 0.75 as particle size increased, representing significant deviations from the theoretical values of 1. The forms of both  $\lambda_{\Omega}$

and  $\mu_\Omega$  are dependent on particle size and effective density and are provided in the work of Johnson et al. [79]. Herein, the forms of these functions determined at low flow conditions ( $0.3 \text{ L min}^{-1}$  aerosol flow) are taken.

### CPMA

The CPMA transfer function used within this work is based on the theoretical particle tracking method of Sipkens et al. [182]. The diffusing transfer function, which is approximated by a smoothed-out trapezoidal function, is given by the following equation

$$\Lambda_{\text{CPMA}} = -\frac{1}{4\delta} [\kappa(G_0(r_2), r_2) - \kappa(G_0(r_1), r_2) - \kappa(G_0(r_2), r_1) + \kappa(G_0(r_1), r_1)], \quad (5.36)$$

where

$$\kappa(G_0(r_{g1}), r_{g2}) = (G_0(r_{g1}) - r_{g2}) \operatorname{erf} \left[ \frac{G_0(r_{g1}) - r_{g2}}{\sqrt{2}\sigma} \right] + \sigma \sqrt{\frac{2}{\pi}} \exp \left[ - \left( \frac{G_0(r_{g1}) - r_{g2}}{\sqrt{2}\sigma} \right)^2 \right]. \quad (5.37)$$

$r_{g1}$  and  $r_{g2}$  are replaced by  $r_1$  and  $r_2$  to evaluate Equation 5.36 accordingly.  $\sigma = \sqrt{2DL/\bar{U}}$  is the diffusive spreading parameter where  $D$  is the particle diffusion coefficient and  $\bar{U}$  is the average flow speed through the classifier.  $G_0(r_{g1})$  is the operator used to map the final radial position,  $r_{g1}$  of the particle to its position at the inlet of the classifier. For a detailed discussion on the derivation of the forms of  $G_0(r_{g1})$ , readers are referred to Sipkens et al. [182]. Within the work, the case specified as 1C described in their work is used, where  $G_0$  takes the form

$$G_0 = r_c + \left( r - r_c - \frac{C_3}{C_4} \right) \exp \left( \frac{-C_4 L}{\bar{U}} \right) - \frac{C_3}{C_4} \quad (5.38)$$

where

$$C_3 = \tau \left( \alpha_\omega^2 r_c + \frac{2\alpha_\omega \beta_\omega}{r_c} + \frac{\beta_\omega^2}{r_c^3} - \frac{qeV}{mr_c \ln(\frac{r_2}{r_1})} \right) \quad (5.39)$$

and

$$C_4 = \tau \left( \alpha_\omega^2 - \frac{2\alpha_\omega\beta_\omega}{r_c^2} - \frac{3\beta_\omega^2}{r_c^4} + \frac{qeV}{mr_c^2 \ln(\frac{r_2}{r_1})} \right). \quad (5.40)$$

$\alpha_\omega$  and  $\beta_\omega$  are parameters related to the angular velocity profile [145, 182].

Experimental validation of the CPMA's transfer function has been undertaken similarly to the AAC by Naseri et al. [133], in which losses and broadening were quantified compared to the theoretical transfer function. However, unlike the AAC transfer function in which the experimentally determined formulation has been used, the use of the theoretical transfer function of the CPMA given by Equation 5.36 has been retained. There are two main reasons for this. Firstly, unlike its theoretical equivalent, the triangular approximation of the CPMA transfer function used in the experimental work of Naseri et al. [133] does not allow the modelling of charge-neutral particles through the CPMA. As will be shown within the results discussion, this can drastically affect measurements when using the CPMA as the upstream classifier. Secondly, unlike the AAC transfer function, which is broader compared to theory, the CPMA's transfer function width was found to be comparable to theory, and only the height (*i.e.*, particle loss) was different.

A final note must be made regarding the method for determining the CPMA classifier speeds and voltages required to select a particle of a given mass. Unlike the single charge operation of the CPMA, which is used in commercial devices, in the present model, particles are unipolarly charged, which means that the speeds and voltage required to select a particle of a desired mass for a given mass resolution are different. Instead, a slightly different method has been used to determine the speed and voltage profile of the CPMA, which takes into account that the aerosol is unipolarly charged; this method is as discussed in Chapter 4, Section 4.2.2. Unless otherwise stated, numerical simulations use a resolution of 3 and a flow rate of 1 L min<sup>-1</sup> to determine the CPMA speed and voltage profile.

## 5.5 Experimental Method

### 5.5.1 MSE Effective Length and transfer function validation

The experimental setup for validating the transfer function of the MSE and determining its effective length (Eq. 5.14) is shown in the top portion of Figure 5.4. Ammonium sulphate particles were produced by atomisation in a Collison nebuliser. Any excess liquid mobilised by the atomisation process was collected in a liquid trap. Particles were subsequently dried by passing them through two diffusion dryers. Particles were then charged by either a Unipolar Diffusion Aerosol Charger (UDAC, Cambustion Ltd.) operated with a  $n_i t$  product

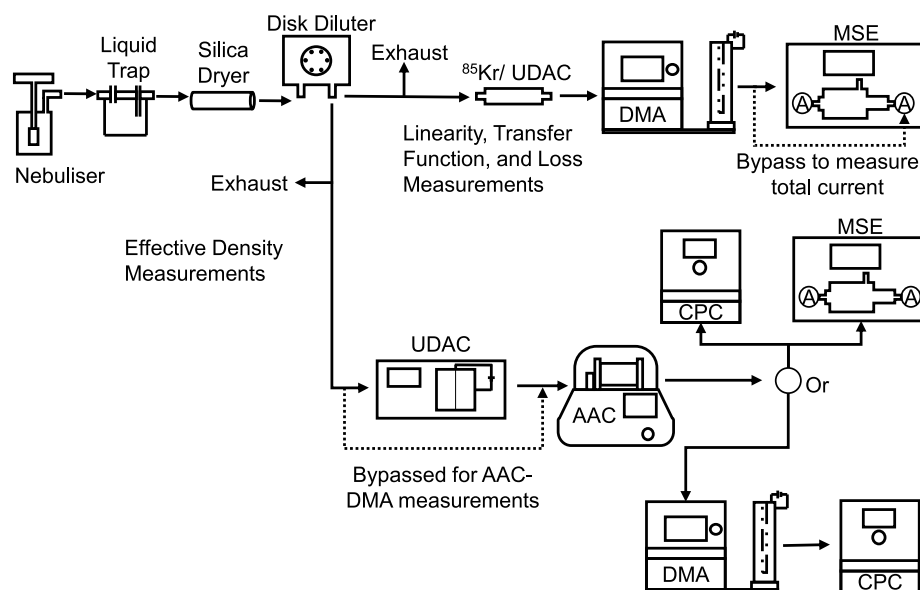


Fig. 5.4 Experimental set-up used to calibrate and validate the transfer function of the MSE. The bottom experimental path depicts the set-up used to measure particle effective density using a tandem UDAC-AAC-MSE-CPC system and an AAC-DMA-CPC.

of  $1 \times 10^{14} \text{ s m}^{-3}$  or a radioactive krypton charger (TSI model 3077a). The use of different chargers enabled characterisation over a wider range of electrical mobilities. Charged particles were then selected by a DMA (TSI Model 3081) operating with a sheath flow rate of  $10 \text{ L min}^{-1}$ , producing a particle sample monodisperse in electrical mobility. Flow rates and voltages of both the DMA and MSE were calibrated using a bubble flow meter (Gilibrator 2, Sensidyne, LP, Clearwater, FL, USA) and a volt meter before measurements were undertaken. The selected particles were then sampled by the MSE. Throughout this work, the sheath flow of the MSE was controlled to  $1 \text{ sL min}^{-1}$  and the aerosol sample flow to  $0.65 \text{ sL min}^{-1}$ . Where  $\text{sL min}^{-1}$  denotes the volumetric flow at a reference pressure of  $101325 \text{ Pa}$  and temperature of  $0^\circ\text{C}$ . For the determination of the effective length, the MSE's closed-loop control was enabled such that the applied voltage was automatically controlled to achieve and maintain balanced current outputs in each electrometer. For each electrical mobility set-point, the voltage that achieved balanced outputs was recorded over 30 s and subsequently averaged. A range of upstream electrical mobilities was chosen to observe linearity between the upstream DMA electrical mobility set-point and the MSE determined average electrical mobility over the range of operating voltages of the MSE. Accurate calibration of the MSE using a DMA is dependent on the DMA resolution (sheath to aerosol flow rate), as well as the upstream charger used (*i.e.*, unipolar vs bipolar). A discussion of the effects of these parameters is described in Section C.1 of Appendix C.

The same experimental setup was then used to determine the MSE transfer function. The total current downstream of the DMA was measured by bypassing the classifier of the MSE and sampling straight into the low-mobility electrometer. The total current was measured every two minutes to ensure the upstream concentration remained stable. Then the sample was passed through the MSE with its PID control now disabled such that the voltage could be manually stepped. At each voltage set-point, the current in both the high and low mobility electrometer was measured for 30 seconds and divided by the total current downstream of the DMA to obtain the transfer probability of each outlet as a function of voltage. The voltage of the MSE was incrementally stepped, and this process was repeated to determine the MSE transfer function as a function of voltage. This was repeated for three different upstream electrical mobility set points.

### 5.5.2 Effective Density

Experimental studies of effective density were conducted in combination with an AAC shown in the bottom portion of Figure 5.4. Particles of DOS and Ammonium Sulphate were generated using an atomiser. The ammonium sulphate aerosol was passed through two diffusion dryers to dry sufficiently. A Cambustion Disk Diluter was used to control the number concentration into the UDAC in order to prevent saturation of the charger for the DOS aerosol. Particles were then selected by the AAC, generating a distribution of particles that are monodisperse in aerodynamic diameter and, therefore, also mobility diameter since the particles have a narrow range of shapes. The classification resolution of the AAC was maintained at 10 for all measurements apart from the measurement of 50 nm ammonium sulphate particles, in which the resolution was reduced to 7.36 due to limitations of classifier speed. Downstream of the AAC, the aerosol was sampled by the MSE in parallel with a CPC (TSI model 3752) operating with flow rates of  $0.65 \text{ sL min}^{-1}$  and  $0.3 \text{ L min}^{-1}$ , respectively. The mobility diameter was determined from the CPC and MSE measurements as detailed in section 5.3.1. To obtain accurate mean charge measurements, the counting efficiency between the CPC and electrometer was calibrated by generating singly charged particles using tandem classification [184]. The results of this are shown in Figure SC.2 in Appendix C. It was found that the CPC under-counted relative to the electrometer by 8.3%. Therefore, a value of  $k = 1.083$  was used when calculating the mean charge using Equation 6.14.

In addition, measurements of effective density were conducted using an AAC-DMA [195] to compare the results between the two methods. An SMPS scan was taken at each AAC set-point, and a Gaussian was fit to the measured distribution in order to determine the average mobility diameter, which was then used in Equation 5.20 along with the AAC set-point to determine the effective density.

## 5.6 Results and discussion

### 5.6.1 Effective Length of the MSE

Determining the effective length of the MSE is important as the classification section is not completely straight, as the flow bends around into the high mobility electrometer (see diagram in Figure 5.1). Thus, an effective length of the classifier needs to be determined using a known electrical mobility. Figure 5.5 shows the MSE-determined electrical mobility, using the actual geometric length of the classification section (46.03 mm), as a function of the upstream DMA set-point. An almost perfectly linear correlation exists between the mobility determined from the MSE and those measured by the upstream DMA electrical mobility set-point ( $R^2 = 0.99$ ), thus suggesting that an effective length is a reasonable approximation. The effective length of the MSE classifier can be determined by multiplying the length of the classifier ( $L = 46.03$  mm) by the gradient of the fitted linear function. Therefore, the effective length of the MSE is  $47.55 \text{ mm} \pm 1.56 \text{ mm}$ .

### 5.6.2 Transfer function Validation

A comparison of the experimentally determined transfer function to the corresponding theoretical values, using the previously determined effective length of 47.55 mm for three particle electrical mobilities, is shown in Figure 5.6. The experimentally determined transfer function of the MSE is in good agreement (average absolute percentage difference between theory and experiment of 8.4% and 4.1% for the high and low mobility transfer functions, respectively) with the theoretical transfer functions of both the high and low-mobility electrometers. The left-hand side of the transfer function is linear, and as such, Equation 5.16 or 5.15 can be used to determine the average particle mobility if the outputs deviate from their prescribed control outputs. There is slight rounding near the corners of the transfer function; this could be due to the lack of true monodispersity (*i.e.*, particles of single electrical mobility) of the sample exiting the upstream DMA as the DMA has a width to its own transfer function [189], allowing particles within a tight band of electrical mobilities to exit the classifier. It could also be due to particle diffusion or adverse flow mixing, which would act to smooth out the sharp edges of the theoretical transfer function. This could be further investigated through finite element methods. The transfer function does not quite reach unity as expected theoretically; this is likely due to losses within the inlet/exit of the MSE. The losses have been measured over a wide range of particle diameters 40 nm to 4000 nm and it was found that the losses were generally less than 3% for most particle diameters. The results of this are shown in Section C.3 of Appendix C.

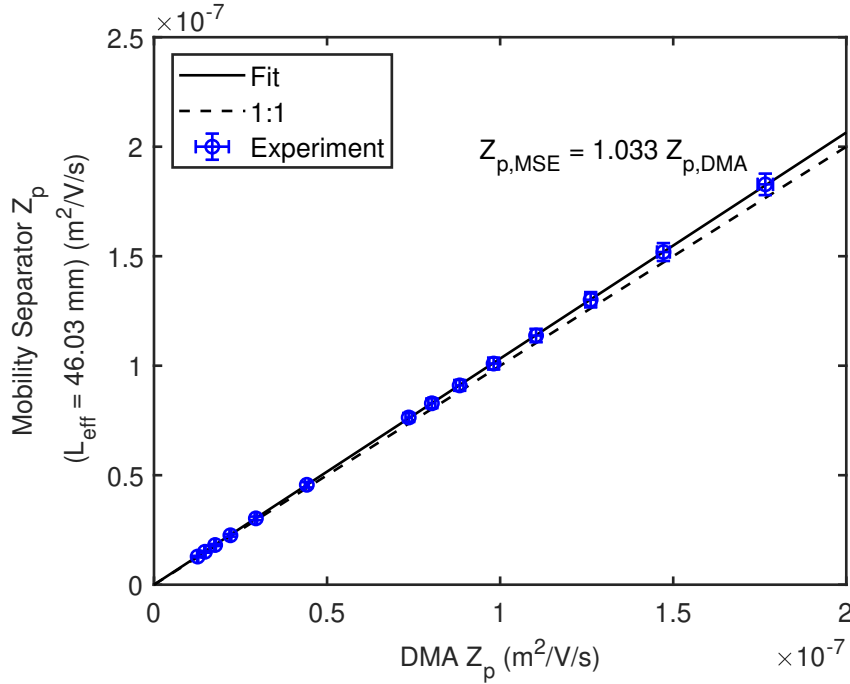


Fig. 5.5 Calibration of the MSE effective length using a DMA. DMA  $Z_p$  is the upstream electrical mobility set-point. The MSE electrical mobility was calculated using an effective length of 46.03 mm. The error bars represent the bias uncertainty in the DMA electrical mobility measurement, estimated to be 1.25% according to Kinney et al. [96]. Error bars in the MSE measurement represent the combination of Type A uncertainties taken as  $1\sigma$  in the average over the measurement and Type B uncertainties of 2.68%, which includes uncertainty in the radii, voltage and aerosol flow rate of the MSE as discussed in Section C.5 of the Appendix C.

### 5.6.3 Numerical Study on Particle Effective Density

#### Calculation of $d_a$ , $d_m$ , $m$ and $\rho_{\text{eff}}$

The ability of a unipolar charger, upstream classifier, MSE, and CPC combination to determine the predicted error of aerodynamic diameter, particle mass, and mobility diameter ( $d_m$ ) relative to the corresponding number-weighted average and effective density of four test aerosols has been numerically assessed using the method outlined in Section 5.3.1. Figure 5.7 shows the results for four test aerosols: DOS, Ammonium Sulphate, Sodium Chloride and Soot. Note that due to the similarity in density and the size distribution used for Ammonium Sulphate (light blue square markers) and Sodium Chloride (red diamond markers) in the numerical model, the results of these aerosols are very similar. The left and right-hand columns in Figure 5.7 correspond to upstream classification by an AAC and CPMA, respectively.

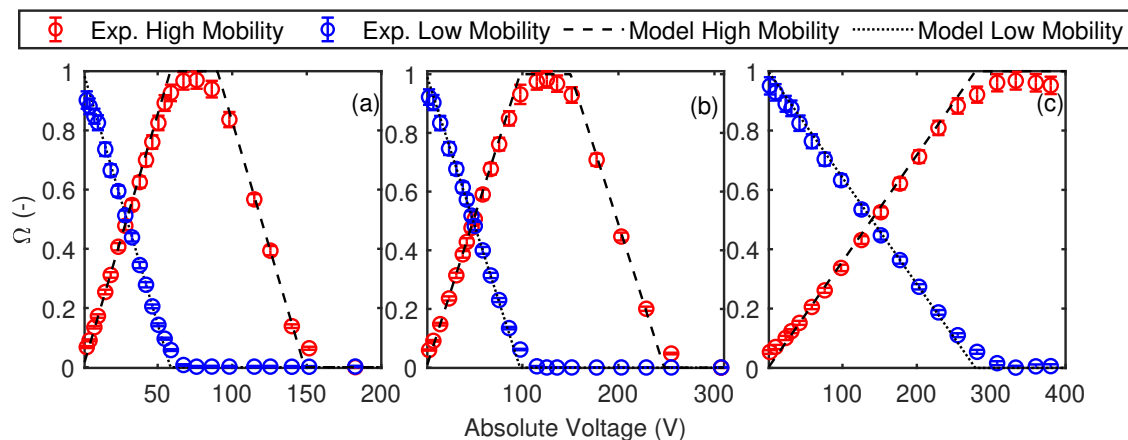


Fig. 5.6 Experimentally measured transfer function compared to the theoretical transfer function with a calibrated effective length. Figures (a), (b) and (c) correspond to upstream DMA electrical mobility set-points of  $1.47 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $3.09 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $8.83 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. Error bars represent the combination of Type A uncertainties taken as  $1\sigma$  over the measurement and Type B uncertainties of 2% or 2 fA in the electrometer signal, whichever was greater for each measurement.

Figure 5.7a shows small errors ( $<5\%$ ) in the ratio of the classification set-point of the AAC and the downstream averaged aerodynamic diameter obtained using Equation 5.26. This means that the aerodynamic set-point of the AAC can be used accurately as a measure of the average aerodynamic diameter downstream of the classifier, with a slight decrease in accuracy below 100 nm where the transfer function broadens due to diffusion. This is unsurprising as the AAC has been shown to accurately size PSL particles over a wide size range [79]. The same can also be said when using the CPMA's mass-to-charge ratio in combination with the average charge of the aerosol population downstream of the CPMA to determine the average transmitted particle mass as shown in Figure 5.7b. However, the determination of the average mass using the combination of the CPMA mass-to-charge set-point and the average charge is more in error at larger sizes. This is due to the interaction between the transfer function of the CPMA and the charge distribution. The distribution of charges drives the range of particle masses that exit the CPMA for a given operating set-point. However, at smaller sizes ( $d_m < 100$ ), particles acquire lower charge states (*i.e.*, 1, 2, 3..) and therefore, the range of masses that have the same mass-to-charge ratio and therefore are classified equally by the CPMA, is broad, owing to the larger relative difference in charge. As the number of charges on the particles increases, the relative difference in charge states is smaller, and as such, the exiting mass distribution is narrower. The exiting mass distribution

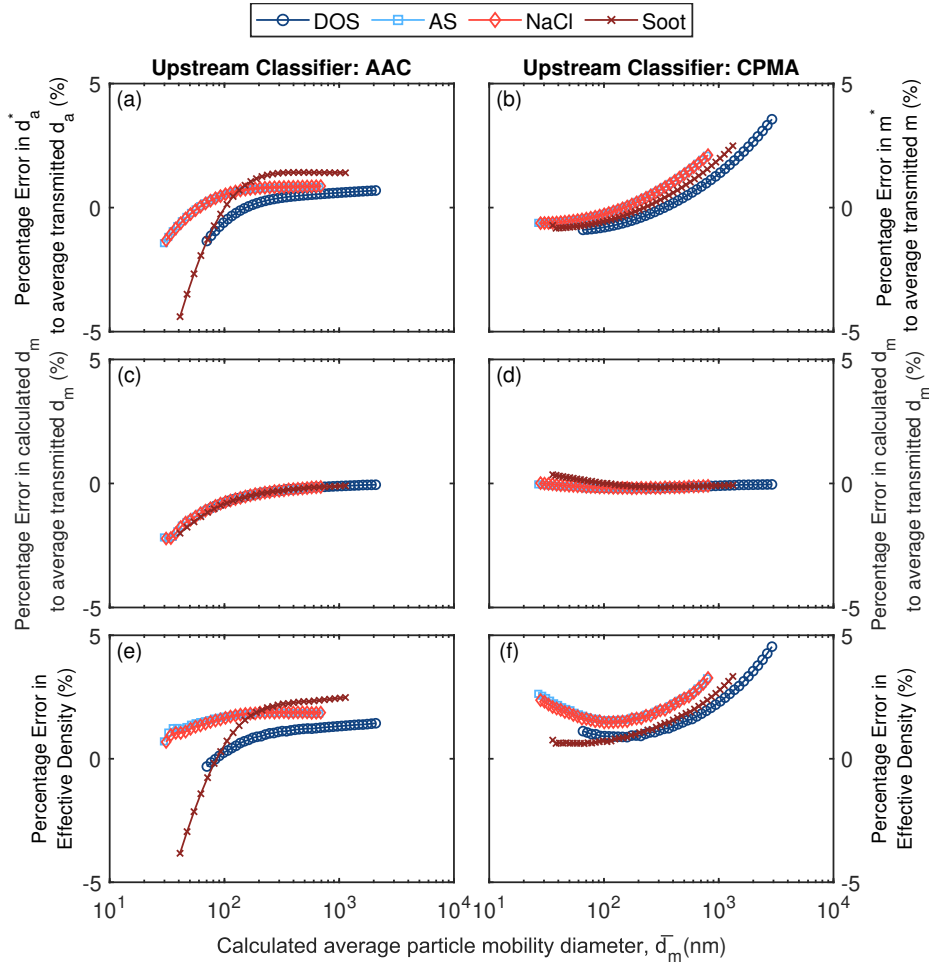


Fig. 5.7 Percentage error in parameters for four different aerosols determined using the calculation methods in section 5.3.1. The left column shows the results in which the upstream classifier is an AAC, the right column where the upstream classifier is a CPMA. Figures (a), (b) show errors in the classifier set-point vs. the number weighted average of the same quantity (*e.g.*,  $d_a$  for the AAC and  $m$  for the CPMA). Figures (c), (d) show errors in the mobility diameter determined using the combination of the average charge and average electrical mobility relative to the number weighted average of the transmitted particles downstream of the upstream classifier. Figures (e), (f) show the errors in effective density relative to the input effective density model for each aerosol as described in section 5.4.2. Note that the x-axis in all plots is the mobility diameter as calculated using the method in section 5.3.1.

when selecting smaller particles can be viewed as discrete peaks located at integer charge states. At larger sizes, the charge peaks blur together, no longer forming distinct charge peaks. This is further confirmed by changing the classifier resolution, which is discussed later in more detail. The extent of error using the CPMA mass-to-charge set-point and average charge to determine the average mass (Eq. 5.24) is less than 5% over the entire size range

investigated. It was demonstrated by Sipkens et al. [180] that the average transmitted mass downstream of a unipolar-particle mass analyser system can be determined to within 30% under a wide variety of experimental conditions, using a series of average charge approaches based on power law fits to more complex charge models. The approach of Sipkens et al. [180] is extremely useful when the necessary experimental facilities to measure the average particle charge are not available. However, where experimental capabilities permit, it is demonstrated in this numerical work that the average transmitted mass downstream of a CPMA can be accurately determined by pairing an electrometer and CPC to obtain the average charge.

For either upstream classifier, the average particle mobility diameter calculated using the MSE average electrical mobility and average charge can be accurately determined to within 2% (Figures 5.7c and d) for all four aerosols. The electrical mobility distribution downstream of each classifier is narrow due to prior classification and unipolar charging. Fuchs' model predicts a nearly linear dependence of particle mobility diameter on the average charge, which means that the electrical mobility distribution is only weakly dependent on particle diameter; as such, the electrical mobility distribution of a unipolar charged aerosol is narrow (See Figure C.1 in Appendix C). These two factors allow for accurate determination of the average electrical mobility using the MSE. Furthermore, this demonstrates that although the aerosol is multiply charged with a distribution of charges and diameters downstream of either classifier, the average charge and average electrical mobility can be used in tandem to accurately determine the average mobility diameter.

The combination of small errors in mass, aerodynamic diameter and mobility diameter results in accurate measurements of effective density as highlighted in Figures 5.7e and f. The estimated error when using either classifier remains within 5% between 30 nm - 3000 nm for aerosols with varying effective density relation and size distributions. This wide dynamic range is beneficial as present tandem methods of measuring effective density are often limited by classification voltages, limiting the maximum particle sizes that can be investigated.

### Sensitivity to model parameters

In practice, the conditions prescribed by the model may not apply to all experimental setups. Therefore, the error in effective density has been investigated when the system is operated under different conditions. In particular, the effect of the charger  $n_i t$  product, classifier resolution, and distribution geometric standard deviation has been investigated. This analysis has been performed solely for the ammonium sulfate aerosol, assuming an effective density constant with particle size and equal to the material density ( $1770 \text{ kg m}^{-3}$ ).

The  $n_i t$  product controls the charger performance, dictating the charge distribution. Figures 5.8a and b show how varying the  $n_i t$  product affects the determination of effective

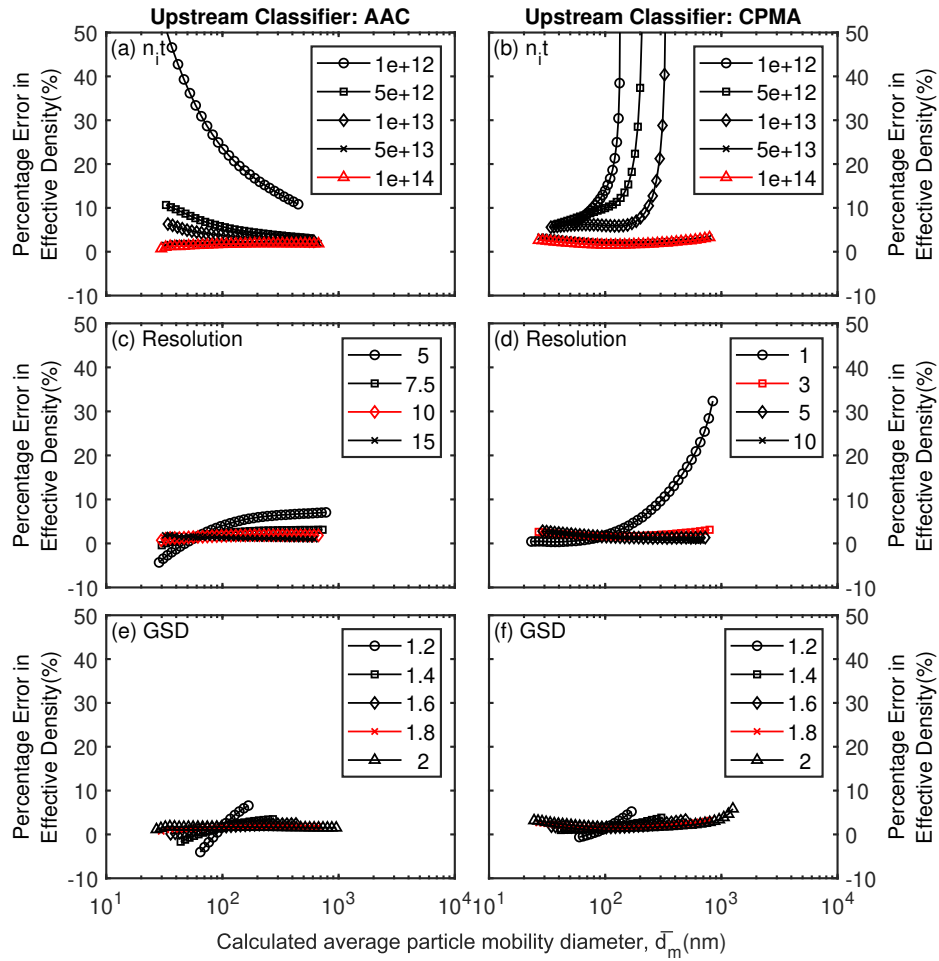


Fig. 5.8 Percentage error in effective density as a function of input model parameters. The left and right hand columns indicate the upstream classifier as the AAC or CPMA, respectively. Figures (a) and (b) show the effect of changes in charge  $n_i t$  product. Figures (c), (d) illustrate the effect of upstream classifier resolution. Figures (e), (f) show the effect of geometric standard deviation. All simulations are for an Ammonium Sulphate aerosol with  $d_g = 100$  nm, and  $N = 1 \times 10^6 \text{ m}^{-3}$ . Baseline simulation conditions which reflect the results for Ammonium Sulphate in Figure 5.7 are shown in red as a reference. Note that the x-axis in all plots is the mobility diameter as calculated using the method in section 5.3.1

density when using the AAC and CPMA, respectively. The effect in reducing  $n_i t$  is markedly different between the two classification methods. As the AAC is a charge-independent classifier, the only factor determining the outlet particle distribution is the particle relaxation time. Therefore, neutral particles only exit the classifier at smaller aerodynamic sizes where neutral particles exist within the size selected population.<sup>3</sup> A CPC counts neutral particles

<sup>3</sup>Note as the charge is mobility diameter dependent the extent to which neutral particles exist downstream of the AAC is dependent on the relation between aerodynamic and mobility size *i.e.*, the particle effective density

but not by an electrometer; therefore, the average charge measurement is under-reported due to the presence of neutral particles. This results in the calculated average mobility diameter determined from Equation 5.25 smaller than the number weighted average, causing an increase in the calculated effective density from Equation 5.20. The errors in effective density are largest at the smallest particle sizes, where the fraction of the classified population that is charge-neutral is greatest and reduces as the number of neutral particles within the size selected population decreases. This effect is alleviated by increasing the  $n_{it}$  product which increases the fraction of smaller particles which attain at least a single charge. For  $n_{it}$  conditions exceeding  $5 \times 10^{13} \text{ s m}^{-3}$ , neutral particles' effect on measurements ceases.

For the CPMA, small neutral particles can exit the classifier depending on the classification conditions. The penetration of small uncharged particles occurs when the CPMA is classifying particles of a larger mass, as the rotational speeds are lower; as such, there is insufficient centrifugal force to remove smaller neutral particles from the flow. At high  $n_{it}$  ( $> 5 \times 10^{13} \text{ s m}^{-3}$ ), the vast majority of particles, even down to 10 nm acquire at least one charge. Therefore, the number of neutral particles is extremely small, which does not interfere with the measurement of the average charge. As the  $n_{it}$  decreases, the fraction of smaller particles remaining uncharged increases, and therefore, the number that exits the upstream CPMA increases. The average mass of the correctly selected particles (*i.e.*, those with the correct mass-to-charge ratios) will be under-estimated by Equation 5.24 as the average charge is under-estimated due to the presence of neutral particles. In addition, as previously stated in the discussion for the AAC, the average mobility diameter determined using Equation 5.25 is smaller than that of the number weighted average of the correctly selected particles due to the incorrect average charge measurement. Referring to Equation 6.18, an underestimation in both mass and mobility diameter results in a competing effect in the calculation of effective density. An under-estimation in mass produces an effective density lower than the true effective density, whereas an under-estimation in mobility diameter results in an effective density higher than the true effective density. However, due to the cubic diameter term, the error in mobility diameter dominates. This results in significant over-estimations in effective density, which can greatly exceed 50% (Figure 5.8b has been truncated to allow for direct comparison with variations in other parameters). The particle size at which these errors in effective density occur becomes increasingly large as the  $n_{it}$  increases and errors become negligible above an  $n_{it}$  product of  $5 \times 10^{13} \text{ s m}^{-3}$ . In practice, the extent to which neutral particles impact the measure of effective density is also a function of the particle size distribution as well as the resolution of the classifier. The exact proportion of neutral particles, and therefore the error caused in effective density for a given classifier set-point, can easily be verified experimentally using an electrostatic precipitator downstream

of the classifier [191]. Ultimately, it is clear that operating with an  $n_it$  product greater than  $5 \times 10^{13} \text{ s m}^{-3}$  reduces the propensity for neutral particles to impact the measurement of effective density when using either an AAC or CPMA.

Figures 5.8c and d show the effect of changing the upstream classifier resolution. The effect of changing the resolution (sheath to aerosol flow rate) of the AAC is marginal, although, as expected, the largest errors occur at lower resolution. Similarly, the CPMA is generally insensitive to resolution ) changes above an  $R_{m,q}$  of 3. However, reducing the resolution to 1 results in an error at larger particle sizes. As alluded to earlier, at smaller sizes (sub  $<100 \text{ nm}$ ), the width of the mass distribution exiting the CPMA is controlled by the charge distribution. Therefore, in this range, the errors at different resolutions approximately collapse onto one another. As the size increases, the mass distribution is more dependent on the width of the CPMA transfer function. Operating the CPMA with an extremely low resolution of 1 results in an overestimation of the average transmitted mass using Equation 5.24 relative to the number weighted average transmitted mass, which increases as particle size increases. The error in effective density can be slightly reduced at larger sizes by increasing the CPMA resolution, as indicated by Figure 5.8d. However, above the nominal resolutions of 10 and 3 for the AAC and CPMA, respectively, the relative reduction in error is rather minimal. Therefore, there is very little benefit in running at increased resolutions. This is important experimentally as increasing the classifier resolution decreases the available measurement size range (due to classifier speed limitations) and reduces the aerosol concentration downstream of the classifier, thereby reducing the electrometer and CPC signal, which would result in greater measurement uncertainty in the average charge and electrical mobility measurements.

The final parameter varied was the distribution geometric standard deviation, which may vary depending on the type of aerosol and generation method used. The errors shown in Figures 5.8e and f exhibit pivoted characteristics about the count median diameter (100 nm) of the distribution with the error in effective density increasing as the GSD decreases. As the GSD decreases, the gradient of the distribution increases such that the distribution becomes sharply changing over the width of the transfer function. This acts to skew measurements in opposing directions on the left and right-hand side of the distribution peak, respectively. However, even though there is a skew, the absolute magnitude of the errors in effective density is lower than 10% for either upstream classifier. Furthermore, distributions with a standard deviation of 1.2 are not typically seen for most common aerosol generation methods unless working with PSL or similar nanoparticles.

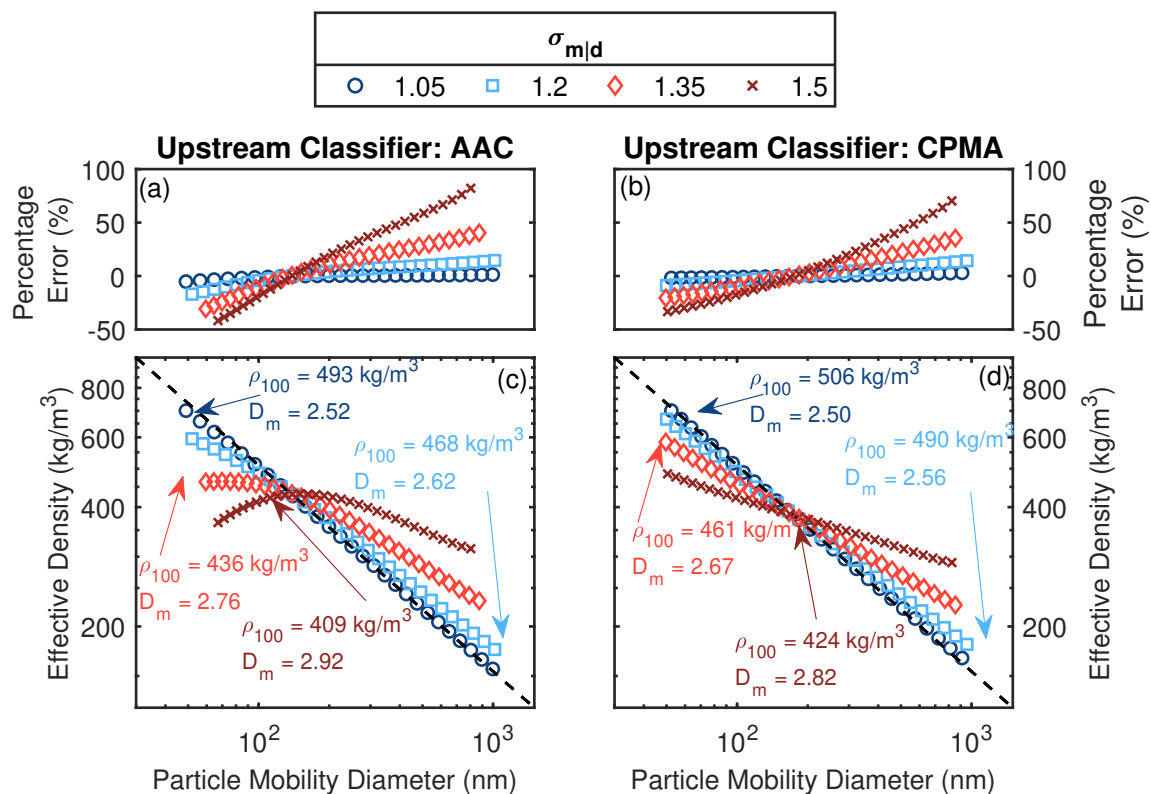


Fig. 5.9 Effective density measured by each tandem system as a function of the geometric standard deviation of the conditional mass width,  $\sigma_{m|d}$ . Figures (a) and (b) indicate the percentage error in the measurement relative to the input effective density relation. Figures (c) and (d) show the effective density relative to the input effective density (black dashed line). Also included is the density constant and exponent obtained through least-squares fitting to the numerically simulated data. Note the density constant  $\rho_{\text{eff},100}$  is abbreviated to  $\rho_{100}$  in the Figure.

## Two-Dimensional Mass-Mobility Distributions

The previous analysis considered single-valued mass-mobility relations in which a one-to-one correspondence between mass and mobility exists. Here, the effects of sampling from a two-dimensional mass-mobility distribution with a varying conditional mass width are discussed. Figure 5.9 shows the effective density determined by the numerical model relative to the input density relation (shown by the black dashed line in each figure), with percentage errors in each column's top panels. As expected for the narrowest width ( $\sigma_{m|d} = 1.05$ ), the conclusions are the same as the analysis using a single-valued mass-mobility relation. However, as  $\sigma_{m|d_m}$  increases, a skew in the density, approximately about the median diameter of the marginal mobility distribution ( $d_g = 150$  nm) is observed in which the effective density measured is lower on the left-hand side and higher on the right compared to the input model.

The trends are relatively similar between each classifier, although the skewing effect is slightly larger when using the AAC as the upstream classifier rather than the CPMA. At the largest conditional mass widths, this results in errors of up to 80%. The resulting skew in effective density has implications for fitting mass-mobility exponents to data of soot aerosols measured using this technique. It is typical to obtain the empirical constants in Equation 5.31 by fitting to the experimental data, which provides the gradient of the relation between mass and mobility in log-log space and a reference particle density/density pre-factor. This enables comparisons of measurements of different sources typically taken at sparsely located points in mass-mobility space, with a wide variety of different instrumentation. Figures 5.9c and d indicate the density parameters obtained through least squares fitting, with each colour corresponding to the geometric standard deviation of the conditional distribution indicated within the legend. Relative to the input model, which uses values of  $\rho_{100} = 510 \text{ kg m}^{-3}$  and  $D_m = 2.48$ , errors in fitted parameters range from 3.3% to -19.8% and -0.7% to -16.8% for the AAC and CPMA, respectively, with the errors increasing as the width of the conditional mass distribution increases. This technique must be used cautiously when inferring mass-mobility values for soot particles with a distribution of masses at a given mobility diameter. To place context on the numerical results here, recent work by Trivanovic et al. [202] has shown that the geometric standard deviation of the conditional mass distribution of soot produced by a variety of fuels was found to lie in the range of 1.2 to 1.4. Therefore, it is likely that the technique proposed here will underestimate fitted density parameters when measuring soot aerosols or other aerosols, which have a range of effective densities at a given size.

The cause of skewing of effective density is elucidated by observing Figure 5.10. Each Figure displays the underlying mass-mobility distribution, illustrated by coloured dashed contour lines. The skew can be explained by examining a simple case for each classifier where the classifier transfer function is considered infinitesimally narrow, such that it appears as a line without any width in mass-mobility space. The AAC selects particles monodisperse in relaxation time. Through Equation 5.18, it can be stated that at a given AAC set-point, the particle mass is inversely proportional to the mechanical mobility (*i.e.*  $m \propto 1/B$ ). This means the AAC transfer function is non-linear in mass-mobility space, in the continuum regime  $m \propto d_m$  and in the free molecular regime  $m \propto d_m^2$ , as shown in Figure 5.10a. It is clear that the intersection of these lines (dotted black lines in Figure 5.10a, labelled 'Transfer Function Approximation' in the legend), which approximate the AAC transfer function, with the contours of the underlying distribution, will act to skew the downstream distribution in opposing directions on either side of the mode of the two-dimensional distribution. A similar argument can be made when using the CPMA as the upstream classifier. At a given CPMA set-point, the mass-to-charge ratio is constant, and therefore, the mass is proportional to

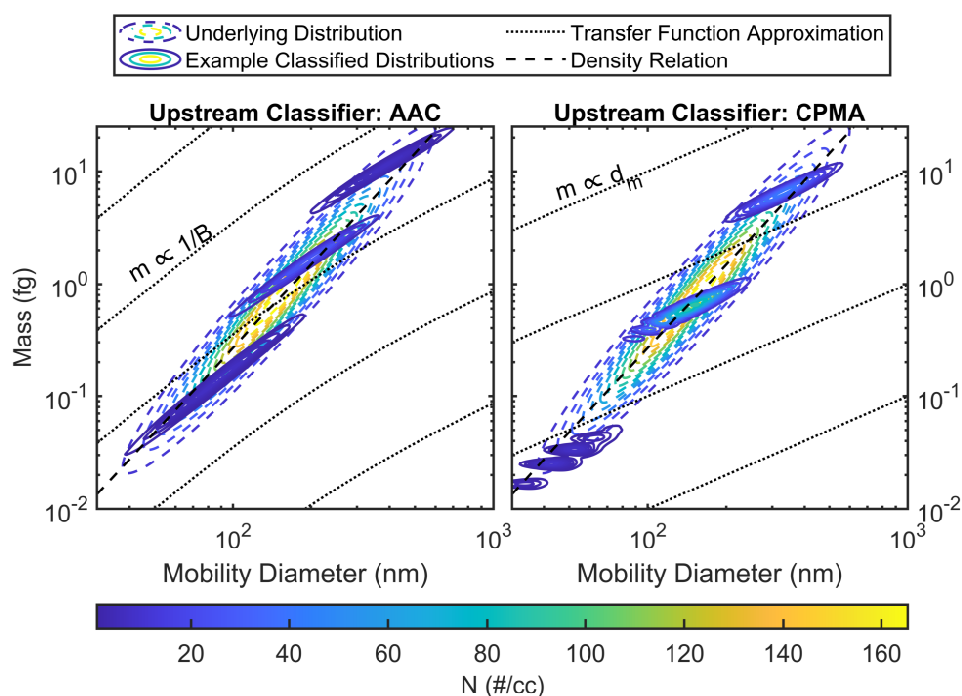


Fig. 5.10 Figure illustrating the cause of skewing in effective density from measurement of a two-dimensional mass-mobility distribution with  $\sigma_{m|d_m} = 1.5$  and geometric effective density relation indicated by the black dashed line ( $k = 0.1168$ ,  $D_m = 2.48$ ). The underlying distribution is shown as contours with dashed lines. The AAC and CPMA transfer function approximations, as discussed in the text, are shown as a dotted line in the Figure on the left and right, respectively. Examples of the distribution downstream of each classifier are shown as solid contour lines.

the particle charge,  $m \propto q$ . Fuchs' charging model predicts a nearly linear relation between average particle charge and mobility diameter,  $q \propto d_m$ . Therefore, at a given CPMA set-point, the particle mass is approximately proportional to the particle mobility diameter  $m \propto d_m$ . In a similar vein, it is clear to see how this will act to skew the measurement from the effective density line. This skewing is illustrated by examples of distributions downstream of each classifier (solid contour lines). The tandem classification method illustrated here measures the downstream population's average (geometric) density, which, if considering an aerosol with a broad distribution of morphologies, does not equate to the underlying distribution's geometric mean relationship.

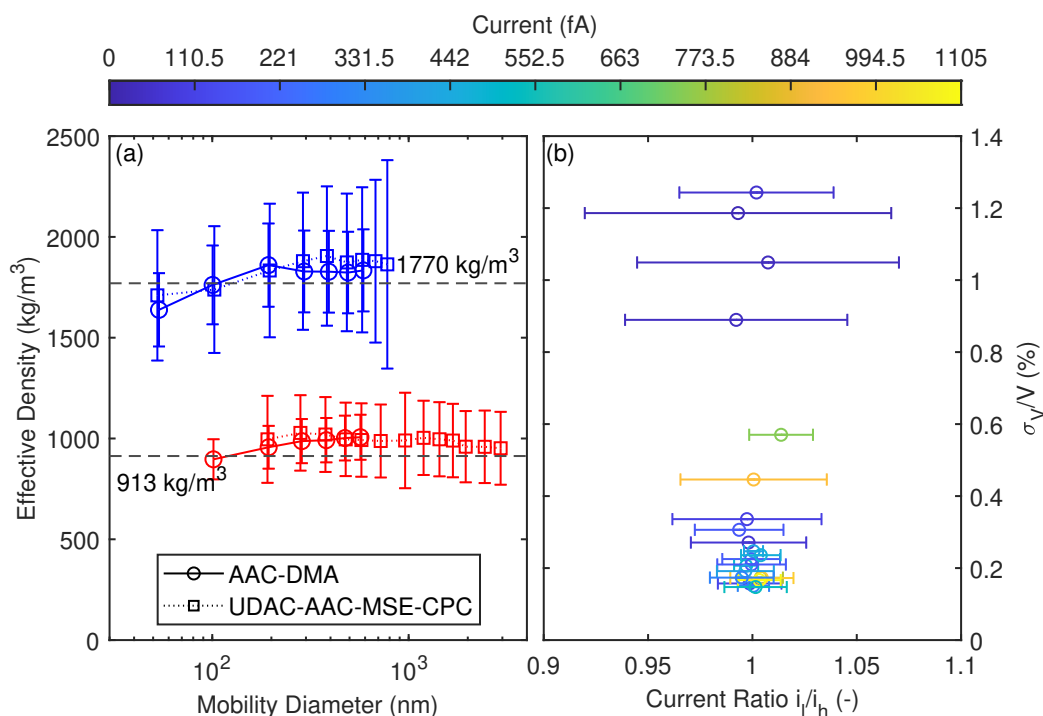


Fig. 5.11 Measurements of (a) effective density of DOS and Ammonium Sulphate using a tandem AAC-DMA (circles) and UDAC-AAC-MSE-CPC system (squares). Error bars for the effective density measurements in (a) include both Type A and Type B uncertainties. Type A uncertainties were taken as  $1\sigma$  over a 60-second measurement, and Type B are calculated according to section C.5 in Appendix C. (b) shows the performance of the MSE in achieving balanced currents as a function of the coefficient of variation in the voltage. Error bars in (b) represent only Type A uncertainties, which were taken as  $1\sigma$  over a 60-second measurement. Colours indicate the total electrometer current, as shown in the colour bar.

#### 5.6.4 Experimental application of the MSE

Measurements of the effective density DOS and ammonium sulphate using a Tandem UDAC-AAC-MSE-CPC system along with corresponding measurements of the same aerosols using an AAC-DMA-CPC are shown in Figure 5.11. The error bars represent the total uncertainty in each quantity, including Type A and B uncertainties. The average effective density of Ammonium Sulphate and DOS measured with the UDAC-AAC-MSE-CPC were determined to be  $1842 \text{ kg m}^{-3}$  and  $989 \text{ kg m}^{-3}$  which is within 8.5% of the bulk density of both materials. The maximum difference between the bulk density and the effective density measurements for any measurement was 13%. This is well within the estimated bias uncertainty of the AAC-MSE classification method, which is  $\sim 18\%$ . Measurements using a tandem AAC-DMA for the same aerosol sources indicate similar errors. However, Tandem AAC-DMA measurements have a bias uncertainty of approximately 11%, less than

that of the UDAC-AAC-MSE-CPC [89]. Although this technique has increased uncertainty relative to conventional tandem arrangements such as the CPMA-DMA or AAC-DMA, the time taken for each measurement is reduced as the downstream measurement of mobility diameter is only dependent on the sampling frequency of the CPC and electrometers within the MSE and does not require a downstream classifier scan or further post-processing of data, thus providing a near real-time measurement of effective density. Another benefit is that effective density measurements of larger-size particles ( $d_m > 700$  nm) can be performed with this new technique, which is not accessible with conventional tandem measurements, typically constrained by the maximum classification voltages due to electric field break-down. However, the available measurement range of effective density measurements for this method is dictated by the available current and concentration signals. In the distribution's tails, accurate measurement may not be possible owing to low particle concentrations. In addition, there may not be sufficient current signal to obtain accurate measurements for smaller particle sizes, as these attain less charge.

Figure 5.11b demonstrates the low-to-high electrometer ratio as a function of the coefficient variation of the voltage for the effective density measurements, which were recorded over a 60 s sampling period. This illustrates the ability of the MSE to achieve balanced outputs between the high and low-mobility electrometer. The average current ratio over all data points is  $1.00 \pm 0.005$ . The coefficient of variation generally remains less than 1%. However, as the current starts to reduce, the voltage varies more over a measurement, resulting in a larger variation in the current ratio. This is due to a decrease in the electrometer signal-to-noise ratio. Therefore, more accurate electrical mobility measurements are obtained with high electrometer signals where they are less affected by measurement noise. The limit of detection of the device is estimated to be  $\sim 30$  fA such that there is  $\sim 15$  fA in each electrometer. This provides an adequate signal such that the electrometer noise does not adversely affect the PID control of the voltage. If particles have a single charge, which will be the case for the smallest particles, a minimum concentration of  $\sim 1.5 \times 10^4 \text{ cm}^{-3}$  would be required.

## 5.7 Conclusions

A novel device, the Mobility Separator Electrometer, has been developed to measure particle electrical mobility with closed-loop voltage control. The theoretically derived transfer function was found to be in good agreement with the experimental measurement once the device was calibrated using an effective length. The power of the MSE arises in tandem applications in which the MSE is combined with existing instrumentation, including a

diffusion charger, up-stream classifier and CPC. Tandem applications have been probed both numerically and experimentally. Numerical simulations show the effective density of a variety of aerosols can be determined to within 5% over a wide measurement mobility diameter range (30 - 3000 nm) without the need for a full deconvolution accounting for the system transfer function, charge distribution and aerosol size distribution. A parametric variation study demonstrated that the presence of uncharged particles can dramatically impact measurements when using the MSE downstream of both an AAC and CPMA, and it is therefore extremely important to operate the diffusion charger with a high  $n_i t$  product ( $> 5 \times 10^{13} \text{ s m}^{-3}$ ) to mitigate the presence of neutral particles in the sampled aerosol population. Further numerical analysis of sampling from a two-dimensional distribution, where a distribution of effective densities can exist at a given size, indicated that the method provides a skewed density measurement. In this case, the errors in the measurement can reach up to 80%.

A tandem UDAC-AAC-MSE-CPC was used experimentally to measure the effective density of DOS and ammonium sulphate. The average effective density of DOS and Ammonium Sulphate was measured to be within 8.5% of the material density.

In terms of operational parameters, the MSE operates with an aerosol flow rate of  $0.65 \text{ sL min}^{-1}$  and a sheath flow rate of  $1 \text{ sL min}^{-1}$ . Under typical conditions, the instrument can measure mobility diameters ranging from 30 nm to 3000 nm, achieving uncertainties of approximately 7% in mobility diameter. However, this level of performance is contingent on careful calibration and is influenced by the distribution of particles being sampled. Additionally, the MSE's sensitivity depends on particle number concentration; it is estimated that a minimum concentration of  $1.5 \times 10^4 \text{ cm}^{-3}$  of singly charged particles is required to produce a sufficiently strong current signal for reliable measurement. Its operation is therefore ill-suited for ambient measurements in which concentrations can be low. The MSE offers real-time measurement of mobility diameter, and effective density when paired with upstream classification. It is therefore, useful in applications in which time sensitivity is an issue such as measurements of aviation-turbine soot in which the cost of operation limits the available measurement time or process engineering checks for powders.

The applications of the MSE in this work demonstrate its use in applications where the particles are pre-classified. The broader application of the MSE remains limited owing to the requirement of narrowly distributed aerosol size, as broad or skewed distributions create problems of interpretation. In the case of a broad distribution, the high mobility detector allows the transmission of many large particles (through the flat region in the transfer function), which skews the point of equal current. Skewed distributions similarly shift the point of equal current. The MSE, therefore, cannot be used as a substitute for a conventional

DMA to measure full polydisperse distributions. The second limitation of the MSE is the requirement of charge correction. The MSE strictly classifies particles by their electrical mobility. Therefore, charge correction is required if the mobility diameter is to be determined. This work shows that this can be done by measuring the average particle charge if a CPC is used in parallel with the MSE. However, if the average charge is not measured, a modelled prediction of the average transmitted particle charge is required to determine the average mobility diameter from the measurement of average electrical mobility. It is, therefore, recommended that the MSE be used in the manner detailed in this work.

## **Chapter 6**

# **Determining Mass Distributions with Unipolar Charger - Particle Mass Analyser Systems: The Mass Mobility Aerosol Spectrometer (M<sup>2</sup>AS) <sup>1</sup>**

### **6.1 Introduction**

The work in both Chapters 4 and 5 details methods for determining average properties of the CPMA classified population; however, they do not address approaches for determining the full mass distribution. As such, the challenge of deducing the sampled mass distribution from count measurements downstream of a unipolar charger-PMA system remains unaddressed. Tackling this issue requires a thorough examination of the limitations associated with measurements using this system and the development of strategies to mitigate them.

The methodology of sequential stages of charging, classification and particle counting is common in aerosol science. A unipolar charger, PMA and CPC could be combined similarly to the SMPS, which combines a bipolar charger, DMA, and CPC [98, 211, 67]. However, as will be shown in this Chapter, there are a number of problems with this methodology. The first issue is having accurate knowledge of the charge distribution. For data correction of raw SMPS measurements, simple regression equations [218, 196] which approximate the steady-state charge distribution attained on an aerosol, are used to determine the particle charge distribution on a particle of a given mobility diameter; these formulations generally apply to a wide range of measurement conditions although there are several scenarios in which

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<sup>1</sup>This chapter is based on a manuscript submitted to Aerosol Science and Technology

they do not hold, which include insufficient residence time within the charger, and charging of non-spherical particles [81, 80, 73, 223]. Through numerical analysis, Leppä et al. [106] demonstrated that the "weak link" in differential mobility analysis is the charge distribution, which holds particularly true for non-spherical particles [81, 123]. Using a numerical approximation, like in traditional electrical mobility analysis, to prescribe the charge on a particle of a given mass in a unipolar-PMA system is likely to introduce errors, and this is an even more pressing issue for mass measurements than for mobility measurements because the particle's effective density, which converts particle mass to mobility diameter [42], adds additional uncertainty in the relationship between the classifier set-point and particle charge, as the charge is considered a property related to an equivalent charging diameter, which is often conflated with mobility diameter [81, 180]. Furthermore, the variation in charge distribution for non-spherical particles when using unipolar chargers is significantly larger than exhibited by bipolar chargers [85, 175, 144, 153].

The second problem relates to determining the transfer function of the CPMA. Particle motion within the CPMA depends on the mass, charge and mobility [145, 182]. With accurate knowledge of these values, the transfer function of the CPMA can be determined, which can then be used to deconvolve measurements. When a particle is spherical, it is easy to convert between mass and mobility if the bulk density of the material is known. However, the mass-mobility relation for arbitrary non-spherical particles can only be determined with additional measurements.

This work aims to illustrate the challenges associated with determining mass distributions using a unipolar charger coupled with a CPMA and CPC (Figure 6.1a) through a numerical model. These challenges arise due to the sensitivity of the system kernel to variations in assumed relations between mass, mobility and charge. To address these issues, a new measurement system called the Mass Mobility Aerosol Spectrometer ( $M^2AS$ ) is introduced. The  $M^2AS$  system, as depicted in Figure 6.1b, incorporates an additional component downstream of the CPMA, namely the Mobility Separator Electrometer (MSE). The MSE, introduced and validated in Chapter 5, integrates differential mobility analysis and current measurement into a single instrument. The MSE uses a sheath flow and a voltage to separate charged particles according to their electrical mobility, much like a DMA [98]. Particles are split between high- and low-mobility outlets, with the charge concentration in each outlet determined by one of two faraday cup electrometers. The voltage that achieves balanced currents between the high- and low-mobility outlets is autonomously adjusted, enabling the determination of the average electrical mobility of the aerosol, pre-classified by the CPMA. This setup enables measurement of the average charge, particle mobility diameter and density downstream of a unipolar charger and CPMA when combined with a CPC. With this additional classifier, it

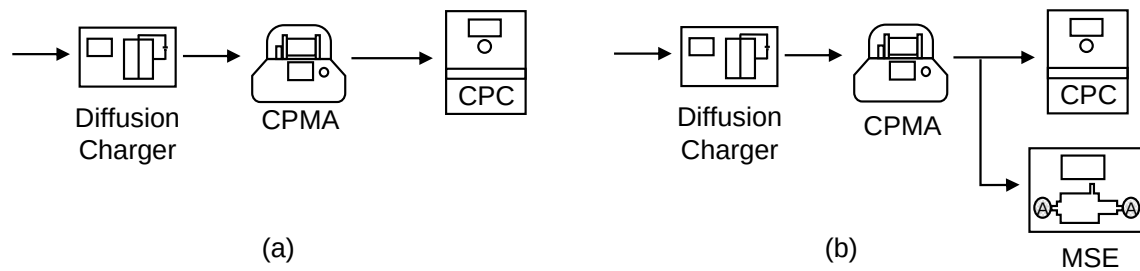


Fig. 6.1 Experimental set-ups applicable for measuring particle mass distributions using a unipolar charger and a CPMA. (a) Only includes measurement of particle concentration using a CPC downstream, whereas (b) illustrates the  $M^2AS$  system, which has all the same components as system (a) but includes an additional classifier downstream, the Mobility Separator Electrometer.

becomes feasible to provide measurements of mass, mobility and charge in a single system, thus enhancing the accuracy of mass distribution determinations. The methodology used to compute the transfer function of the  $M^2AS$  is elaborated upon, and the advantages of incorporating additional measurements from the MSE in determining mass distributions are demonstrated. Specifically, numerically generated mass distributions obtained via data inversion using the unipolar diffusion aerosol charger–CPMA–CPC system (UDAC-CPMA-CPC; Figure 6.1a) are compared with those obtained using the  $M^2AS$  under perturbed simulation conditions. These perturbed conditions are designed to replicate scenarios in which the mass, mobility, and charge of the measured aerosol deviate from expected values. Additionally, scenarios where the  $M^2AS$  may not be a suitable measurement technique are identified. It is important to note that this study is purely numerical and does not include experimental validation of the full  $M^2AS$  system.

## 6.2 Aerosol Mass Distribution Measurements: The Forward Model and Inversion Problem

### 6.2.1 Kernel

The probability that a particle with given characteristics transmits through the system to a downstream detector, as shown in Figures 6.1a and b, is determined by a series of device transfer functions. In unipolar charger-CPMA-CPC systems <sup>2</sup>, the overall kernel is given by

<sup>2</sup>The counting efficiency of the CPC is taken as unity throughout this work

the product of the unipolar charger transfer function and the CPMA transfer function. The kernel at a given measurement point, indexed as  $i$ , is expressed as:

$$K_i(m, d_m) = \sum_{q=0}^{q_{\max}} f_q(q, d_m, \mathbf{p}_i) \Omega(s_i^*, m, d_m, q, \mathbf{p}_i) \quad (6.01)$$

where  $f_q(q, d_m, \mathbf{p}_i)$  represents the fraction of particles with mobility diameter  $d_m$  that have an integer charge state  $q$ . The sum of these charge fractions for a given diameter equals one. The function  $\Omega(s_i^*, m, q, d_m, \mathbf{p}_i)$  denotes the transfer function of the CPMA at the  $i$ th mass-to-charge set-point,  $s_i^*$ , which depends on the particle mass ( $m$ ), charge state ( $q$ ), and mobility diameter ( $d_m$ ). The vector  $\mathbf{p}_i$  denotes the additional operating parameters required to describe each device's transfer function. For the unipolar charger, these include ion and gas properties, particle conductivity, and the ion-concentration time product ( $n_i t$ ) of the charger. For the CPMA, relevant parameters include physical settings such as rotational speed ( $\omega$ ), voltage ( $V$ ), and aerosol flow rate ( $Q$ ), as well as gas conditions like temperature and pressure.

The particle charge distribution for a unipolar charger is commonly evaluated using the work of Fuchs [49]. The CPMA transfer function can be calculated using the analytical particle tracking method of Sipkens et al. [182] as described by Equations 5.36 to 5.40 in Chapter 5.

### 6.2.2 The Forward Problem

The forward problem<sup>3</sup>, which determines the particle counts measured by a particle counter at the  $i^{\text{th}}$  measurement point, is described by taking a convolution of the kernel with the true underlying distribution,  $n(m, d)$ ,

$$N_i = \int \int K_i(m, d_m) n(m, d_m) \text{dlog } m \text{dlog } d_m + \varepsilon_i \quad (6.02)$$

where  $\varepsilon_i$  is the error in the  $i^{\text{th}}$  measurement. To evaluate the forward model a formulation of the distribution function,  $n(m, d_m)$  is required. Particle size distributions are often represented by a lognormal distribution of a single parameter. For instance, the number-weighted mass distribution could be represented by

$$n(m) = \frac{\text{d}N}{\text{dlog } m} = \frac{N_{\text{tot}}}{\sqrt{2\pi \log^2 \sigma_m}} \exp \left( -\frac{(\log m - \log m_g)^2}{2 \log^2 \sigma_m} \right) \quad (6.03)$$

<sup>3</sup>Some of the definitions in this section are repeated from Chapter 5 to give better context to the reader

where  $N_{\text{tot}}$  is the total aerosol concentration,  $\sigma_m$  is the geometric standard deviation, and  $m_g$  is the geometric mean mass. A lognormal distribution function is often combined with an effective density relationship, which enables conversion between particle property spaces, such as from mass to mobility or aerodynamic diameter [42]. This relation is often represented by a power law given by [128]

$$\rho_{\text{eff}} = k d_m^{(D_m-3)}, \quad (6.04)$$

where  $k$  and  $D_m$  are named the mass-mobility pre-factor and exponent, respectively. This relation is commonly phrased in terms of the effective density of a 100 nm mobility-sized particle,  $\rho_{\text{eff},100}$  as

$$\rho_{\text{eff}} = \rho_{\text{eff},100} \left( \frac{d_m}{100 \text{ nm}} \right)^{(D_m-3)}, \quad (6.05)$$

to provide an anchoring point for the relationship. It should be noted that this equation assumes that the mass-mobility relation is single-valued, meaning that a particle of a given mass only maps to a single mobility value. Whilst assuming single-value mass-mobility relation is correct for spherical aerosols, this is not true for morphologically diverse aerosols such as soot [202, 178, 161]. As demonstrated by the kernel denoted by Equation 6.01, the transmission of particles through a unipolar charger-CPMA system is dependent on particle mass, mobility diameter and charge (which is assumed to be mobility diameter dependent), and it is therefore not sufficient in a numerical model to consider a lognormal mass distribution with a single-valued power law relation to evaluate the forward model. Therefore, a two-dimensional mass-mobility distribution needs to be considered. A two-dimensional formulation of the particle size distribution presents a more accurate representation of the underlying particle distribution for particles with a range of morphologies at a given mass [178, 161]. Here, the underlying distribution is represented by a two-dimensional lognormal distribution, as done in Chapter 5

$$n(m, d_m) = \frac{\partial^2 N}{\partial \log d_m \partial \log m} = \frac{N_{\text{tot}}}{2\pi \log \sigma_{d_m} \log \sigma_{m|d_m}} \exp \left( -\frac{(\log d_m - \log d_g)^2}{2 \log^2 \sigma_{d_m}} - \frac{(\log m - \log m_g | d_m)^2}{2 \log^2 \sigma_{m|d_m}} \right). \quad (6.06)$$

$\sigma_{d_m}$  is the standard deviation of the marginal mobility distribution,  $d_g$  is the count median diameter.  $\sigma_{m|d_m}$  is the geometric standard deviation of the mass distribution conditional on a

given mobility diameter.  $\sigma_{m|d_m}$  is assumed to be independent of particle mobility diameter (*i.e.* taken as a constant parameter). The geometric mean mass at a given mobility diameter,  $m_g|d_m$ , can be calculated from the effective density relation as follows

$$m_g|d_m = \frac{\pi}{6} \rho_{\text{eff,g}} d_m^3 \quad (6.07)$$

where  $\rho_{\text{eff,g}}$  can be determined from Equation 6.05.

Therefore, the distribution in log-log mass-mobility space is centred around a line of gradient  $D_m$ , with the geometric standard deviation of the conditional mass distribution dictating the spread about the line. Equation 6.06 can be integrated across all mobility diameters to obtain the marginal mass distribution given by Equation 6.03. The geometric standard deviations of the marginal mobility distribution, marginal mass distribution and the conditional mass distribution are related by the following

$$\log^2 \sigma_{d_m} = \frac{\log^2 \sigma_m - \log^2 \sigma_{m|d}}{D_m^2} \quad (6.08)$$

### 6.2.3 The inversion problem

The inverse problem aims to obtain the distribution function from particle count measurements. Whilst this would normally detail finding the distribution function defined in the forward problem, there is a slight nuance here due to the choice of a two-dimensional distribution representing the underlying distribution. Tandem measurement techniques which place two different aerosol classifiers in series with one another followed by a particle counter (*e.g.* a CPMA followed by a SMPS) can be used to determine the full mass-mobility distribution (Equation 6.06) as the classified distribution is measured across two property domains [182, 161, 202, 132]. A single classifier cannot be used in the same manner as there is insufficient information from measurements in just one domain (in the case of the CPMA, this is particle mass). Therefore, for the systems in Figure 6.1, the inverse problem reduces to the case where the objective is to obtain only the mass distribution.  $n(m)$ , from particle count measurements and a single-value power law relation (*e.g.* Equation 6.05) is used to relate particle mass to mobility diameter to evaluate the inversion kernel. The particle concentration at the  $i^{\text{th}}$  measurement point follows

$$N_i = \int K_i(m) \frac{dN}{d \log m} d \log m + \varepsilon_i. \quad (6.09)$$

In practice, Equation 6.09 is discretised into  $j$  finite elements and approximated as follows

$$N_i \approx \sum_{j=1}^{j=k} K_i(m_j) \left. \frac{dN}{d \log m} \right|_{m_j} (\Delta \log m)_j + \varepsilon_i. \quad (6.10)$$

For all  $i$  measurement points, this forms a system of linear equations which can be written succinctly as

$$\mathbf{N} = \mathbf{A}\mathbf{x} + \boldsymbol{\varepsilon} \quad (6.11)$$

where  $\mathbf{N}$  is a vector of particle concentration measurements equal in length to the number of measurements taken,  $\mathbf{A}$  is the discretised kernel, and  $\mathbf{x}$  is the distribution function, which is the quantity that to be obtained. The problem of inversion has been tackled by many authors who have developed a multitude of techniques to obtain accurate reconstructions of particle size distributions [88, 209, 181]. The purpose of this work is not to identify the best inversion technique to determine particle mass distributions but rather to demonstrate how additional measurements made by the M<sup>2</sup>AS with the addition of the MSE (see Section 6.3.3) help to produce more accurate reconstructions when the sampled aerosol deviates away from an assumed mass-mobility relation and charge distribution. Throughout this work, the commonly used weighted first-order Tikhonov regularisation is employed, which introduces an additional regularisation term to the least-squares approach,

$$\mathbf{x} = \arg \min_x (||\mathbf{W}(\mathbf{A}\mathbf{x} - \mathbf{N})||_2^2 + \lambda ||\boldsymbol{\Gamma}\mathbf{x}||_2^2), \quad (6.12)$$

where  $\mathbf{W}$  is a weighting function that weights the data by the reciprocal of the variance in particle counts.  $\boldsymbol{\Gamma}$  is the Tikhonov matrix, which in this work is a first difference operator, and  $\lambda$  is a constant that controls the degree of regularisation.  $||\cdot||_2^2$  is the square of the euclidean norm. To determine  $\mathbf{x}$ , the system kernel ( $\mathbf{A}$ ) needs to be determined. The process of determining the system kernel and generating synthetic data for the configurations in Figures 6.1a and b are discussed in the following sections.

## 6.3 Determining the kernel for inversion

### 6.3.1 Determining the kernel for a UDAC-CPMA system

To evaluate the kernel given in Equation 6.01, the charge distribution and CPMA transfer function have to be evaluated. The CPMA transfer function is evaluated as described in Equation 5.36. For the case of the unipolar charger-CPMA-CPC system, the charge distribution is determined using the model of Fuchs [49]. Conversion from particle mass

to mobility is required to evaluate the charge distribution and the CPMA transfer function. This is done assuming a single-valued mass-mobility relation as in Equation 6.05. As this is information not known apriori or would require additional equipment to measure values of  $\rho_{\text{eff},100} = 510 \text{ kg m}^{-3}$  and  $D_m = 2.48$ , which are average values obtained from fitting to a range of soot data [147], are assumed. Furthermore, it is assumed the simulated charger is operated at an  $n_{it}$  product of  $1 \times 10^{14} \text{ s m}^{-3}$ . The main purpose of this work is to evaluate how sensitive inversion is to assumptions of these values, which in practice may differ relative to the aerosol being measured.

### 6.3.2 Determining the kernel of the M<sup>2</sup>AS

As the components upstream of the CPC are the same in the UDAC-CPMA system and M<sup>2</sup>AS (Figures 6.1a and b), the inversion kernel could be evaluated in the same manner described for the UDAC-CPMA-CPC system. However, the additional measurements provided by the MSE enable calculations that constrain both the mass-mobility relation and particle charge distribution. Therefore, no assumptions about these quantities needed.

### 6.3.3 Calculation of mean charge, mobility diameter and average effective density

For clarity, this section repeats the determination of average quantities from a CPMA-MSE-CPC detailed in Chapter 5. The following calculations are made at each step of a M<sup>2</sup>AS measurement; therefore, a vector of quantities equal in length to the number of measurements is formed. The subscript  $i$  denotes that each of these quantities is evaluated at the  $i^{\text{th}}$  measurement point. The CPMA mass to charge setpoint at the  $i^{\text{th}}$  measurement point is given by;

$$s_i^* = \frac{m}{q} = \frac{eV}{w_c^2 r_c^2 \ln(\frac{r_2}{r_1})} \quad (6.13)$$

The average charge is obtained from the ratio of total MSE current to CPC signal

$$\bar{q}_i = \frac{i_h + i_l}{NQ_a e}. \quad (6.14)$$

Where  $i_h$  and  $i_l$  are the currents measured in the high and low mobility channels of the MSE, respectively. Note that the MSE operates such that high and low mobility currents are balanced such that  $i_h = i_l$  to determine the average particle electrical mobility.  $Q_a$  is the MSE

sample flow rate, and  $N$  is the number concentration measured by the CPC. The average particle mass can be calculated by multiplying Equation 6.13 by 6.14

$$\bar{m}_i = s_i^* \bar{q}_i. \quad (6.15)$$

The MSE splits particles between high and low-mobility outlets. The average particle of electrical mobility is measured by satisfying the condition that high and low-mobility electrometers measure equal currents. The average particle electrical mobility, determined in Chapter 5 is given by

$$\bar{Z}_{pi} = \frac{-Q_a \ln(\frac{r_2}{r_1})}{4\pi LV^*}. \quad (6.16)$$

where  $V^*$  is the voltage that balances the currents between the high and low mobility electrometers in the MSE, and  $r_2$ ,  $r_1$  and  $L$  are the outer radii, inner radii and classifier length, respectively. The average particle mobility  $\bar{Z}_p$  is related to the average particle mobility diameter  $\bar{d}_m$  and average charge by

$$\bar{Z}_{pi} = \frac{\bar{q}_i e C_c(\bar{d}_{mi})}{3\pi\mu\bar{d}_{mi}} \quad (6.17)$$

where  $e$  is the charge on an electron,  $\mu$  is the air viscosity and  $C_c(\bar{d}_{mi})$  is the Cunningham slip correction factor [93]. The average particle mobility diameter can be solved iteratively by substituting Equations 6.14 and 6.16 into Equation 6.17.

The average effective density of a particle is given by the mass of the particle divided by the volume of an equivalent sphere with the same mobility diameter as the particle,

$$\bar{\rho}_{eff_i} = \frac{6\bar{m}_i}{\pi\bar{d}_{mi}^3}. \quad (6.18)$$

By substituting values of average mass and average mobility diameter into Equation 6.18, an estimate for the average particle effective density is acquired.

### 6.3.4 Evaluation of the Mass-Mobility relation and Charge distribution in the M<sup>2</sup>AS

Unlike the unipolar charger-CPMA-CPC system, assumptions about the mass-mobility relation or charge distribution are avoided in M<sup>2</sup>AS measurements, thanks to the additional data on average charge, average mass, and average mobility diameter. The measurements of mass and mobility can be fit to Equation 6.05 through least squares minimisation to obtain

estimates for both  $\rho_{\text{eff},100}$  and  $D_m$ . Figure 6.2a shows an example of this for synthetically generated data. The error bars in this synthetically generated data are obtained through additional noise terms discussed in later sections. The uncertainties are larger at the smaller and larger particle sizes where the electrometers and CPC counting noise are typically greater owing to the reduced concentrations of particles in the tails of the distribution. The determined mass-mobility constants are then used to enable conversion from particle mass to mobility to evaluate other functions.

Measurement of the mean charge as a function of the average particle mobility diameter provides a pseudo-direct measurement of the particle charge distribution. To enable estimation of the mean particle charge for any particle size, the following function is fit, using least squares regression, to the measurements of mobility diameter and mean charge

$$\bar{q}(d_m) = a_q d_m^2 + b_q d_m + c_q. \quad (6.19)$$

A quadratic fit is used to model diffusion and field charging, which scale approximately with particle diameter and surface area, respectively [70]. Chargers can exhibit some field charging if the aerosol is exposed to an electric field [18]. However, in this numerical work, Fuchs' model is used to evaluate the charge distribution in the forward model, which neglects any field charging. Therefore, a power law function could equally be fit data [140, 180]. However, as this inversion method is intended for experimental systems where there may be some element of field charging, the quadratic term is retained. An example fit is shown in Figure 6.2b, note that  $a_q$  is extremely small. Equation 6.19 only determines the mean charge per particle for a given particle mobility diameter. However, the charge distribution variance or width is also important, given the CPMA classifies particles by their mass-to-charge ratio. This means, for example, that a particle of high mass may have a larger charge such that it classifies the same as a particle of smaller mass with its average charge. Therefore, it is necessary to calculate the width, defined here as  $\sigma_q$ , of the charge distribution for each particle diameter. This quantity is not directly measurable within the M<sup>2</sup>AS system, requiring more extensive measurement procedures [81, 80], and as such, the charge distribution width has to be assumed from a model. The model of Fuchs [49] is used to determine the charge distribution variance at 30 logarithmically spaced points from the minimum to the maximum mobility diameter measured. To determine the charge distribution width, Fuchs' model is evaluated at the  $n_i t$ , which minimises the difference between the charge predicted by Equation 6.14 and the charge determined by Fuchs' model. The calculated charge standard deviation points are fit to the following function

$$\sigma_q(\bar{q}) = a_\sigma \bar{q}^{b_\sigma}. \quad (6.20)$$

which enables the calculation of the charge distribution width (Example shown in Figure 6.2c). The charge distribution on a particle of mobility size,  $d_m$ , is then calculated assuming a Gaussian profile given by

$$f_{q,\text{gauss}}(d_m) = \frac{1}{\sigma_q \sqrt{2\pi}} e^{-(q-\bar{q})^2 / 2\sigma_q^2}. \quad (6.21)$$

The kernel used for inverting M<sup>2</sup>AS data is still based on the analytical form of the CPMA transfer function. However, the charge distribution is replaced with Equation 6.21, and the mass-mobility constants are derived from direct fits to the measurements.

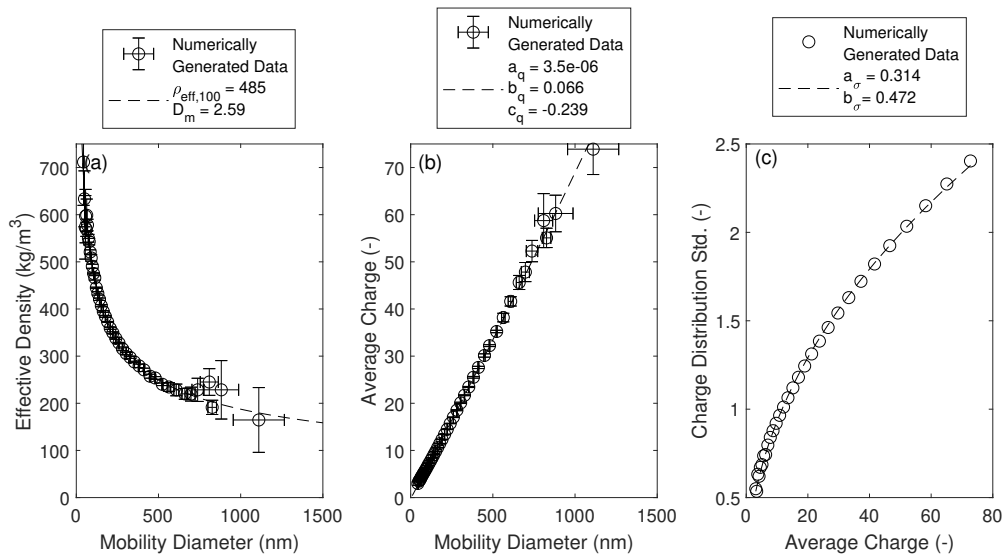


Fig. 6.2 Figure demonstrating generated synthetic data obtained through the numerical model of Chapter 5 for the M<sup>2</sup>AS. Figure (a) demonstrates noise-corrupted measurements of effective density, (b) noise-corrupted measurements of average charge and (c) width of particle charge distribution obtained from Fuchs' model [49]. The dashed lines indicate fits according to equations 6.05, 6.19 and 6.20 in Figures (a), (b) and (c), respectively. Note that there are no error bars included in Figure (c), as the calculation of the charge distribution width comes directly from a numerical model.

### 6.3.5 Conversion from number weighted mass distributions to number weighted -aerodynamic, number weighted- mobility and mass-weighted distributions

The determined mass distribution in logarithmic space can readily be converted from a given property space to another with knowledge of the effective density of the particle.

Therefore, in theory, the fitted effective density relation (Figure 6.2a) obtained through M<sup>2</sup>AS measurements can be used to convert from mass to mobility or aerodynamic space, thereby obtaining the corresponding distribution in that property space. The lognormal mobility distribution can be obtained from the lognormal mass distribution using the following equation,

$$\frac{dN}{d\log d_m} = \frac{dN}{d\log m} \frac{d\log m}{d\log d_m} = \frac{dN}{d\log m} \cdot D_m. \quad (6.22)$$

The mobility distribution can be converted to an aerodynamic distribution through,

$$\frac{dN}{d\log d_a} = \frac{dN}{d\log d_m} \frac{d\log d_m}{d\log d_a} \quad (6.23)$$

where  $\frac{d\log d_m}{d\log d_a}$  can be evaluated using the method of Johnson et al. [79]. A mass-weighted distribution can also be obtained by multiplying the number-weighted mass distribution by the particle mass

$$\frac{dM}{d\log m} = \frac{dN}{d\log m} \cdot m. \quad (6.24)$$

## 6.4 Synthetic data generation and analysis

### 6.4.1 Aerosol Distribution

To evaluate the quality of the inversion algorithms corresponding to the two different systems in 6.1(a) and (b), synthetic data for particle counts (i.e. vector  $N$  in equation 6.11) at each CPMA set-point (speeds and voltages), as well as measurements of average charge and average mobility diameter, were generated data using the numerical model described in Chapter 5. This was performed using open-source MATLAB code developed by Sipkens et al. [181]. For the two-dimensional formulation of the underlying distribution, the parameters of the marginal mass distribution ( $m_g$ ,  $\sigma_m$ ) were fixed along with the conditional mass distribution width ( $\sigma_{m|d}$ ) and therefore, the parameters of the marginal mobility distribution ( $d_g$ ,  $\sigma_{d_m}$ ) were calculated based on the choice of the conditional mass width as well as the geometric mean effective density relation of the aerosol. For all simulations, the total particle concentration was fixed at  $1 \times 10^6 \text{ cm}^{-3}$ . An example of the distribution used to evaluate the forward model is shown in Figure 6.3. The surface plot shows the full two-dimensional distribution, whilst the distributions on either side represent the marginal distribution in mass and mobility space. The marginal mass distribution, shown as a black dashed line, is the quantity that is being sought through inversion.

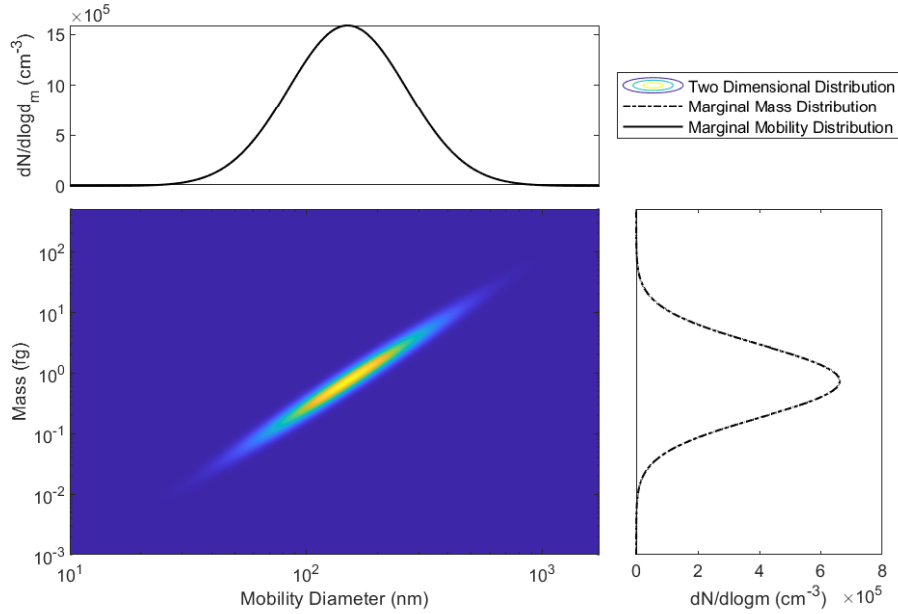


Fig. 6.3 Example distribution used to evaluate the forward model in this work. The marginal mass distribution, shown as a black dashed line, is the quantity that is being sought through inversion.

The distribution parameters were chosen arbitrarily, with variables selected to resemble those of a combustion aerosol having count median mass,  $m_g$ , of 0.73 fg and  $\sigma_m$  of 4. The width of the conditional mass distribution,  $\sigma_{m|d}$  was initially allowed to vary between 1.1 and 1.5 to evaluate the effect of using a single-valued density relation, described by Equation 6.05, to invert data that is sampled from a distribution that has a range of density values. The final parameters used to characterise aerosol morphology, and subsequently the rest of the distribution parameters, are  $\rho_{\text{eff},100}$  and  $D_m$ . The default values of these parameters were taken as  $510 \text{ kg m}^{-3}$  and 2.48, but both were allowed to vary within this study, as discussed in Section 6.4.3. From these morphological parameters and the prescribed mass distribution parameters, the geometric mean diameter,  $d_g$ , and geometric standard deviation,  $\sigma_{d_m}$ , can be calculated.

### 6.4.2 Noise Affected Data

The forward model given by Equation 6.02 provides particle count data void of noise and does not reflect actual experiments. Synthetic noise has been added to the data generated by the forward model to better mimic experimental measurements. It is assumed that the noise in the counts derived from a CPC (*i.e.*  $N_i$ ) can be modelled by a Poisson-Gaussian

noise model. CPC counts can be modelled as independent counting events, making a Poisson distribution an ideal candidate to represent them statistically. With sufficiently large counts, the Poisson distribution can be modelled as a normal distribution with mean equal to zero and variance equal to the number of particle counts. Additional Gaussian noise is added (not the same as Poisson noise approximated as normally distributed), representing fluctuations in aerosol source or electronic noise in the CPC. This is taken as 0.01% of the peak count.

To model the additional component of the MSE used within the M<sup>2</sup>AS, the model described in Chapter 5 is utilised, which enables calculation of the average electrical mobility by finding the voltage which provides balanced currents in the high and low mobility electrometers in the device. Electrometers measuring fempto-ampere-sized currents are particularly sensitive and are assumed to exhibit noise approximated as signal-independent Gaussian noise with a standard deviation of 2 fA. Note that electrometer noise affects the measurement of mean charge and the electrical mobility measurement, which seeks to balance the electrometer currents. The model detailed in Chapter 5 provides the voltage,  $V^*$ , which balances currents into the high and low mobility electrometers based on the theoretical transfer function of the MSE. To add noise to this measurement, the MSE set-point is considered to be able to instantaneously change to balance outputs in response to noise added to each electrometer signal. The noise-affected voltage,  $V_{\text{noisy}}$ , can then be calculated from

$$V_{\text{noisy}} = V^* \left( 1 + \frac{\varepsilon_l - \varepsilon_h}{i_h + i_l} \right) \quad (6.25)$$

where  $\varepsilon_l$  and  $\varepsilon_h$  are the signal-independent Gaussian noise in the low and high electrometer signals. To mimic experiments, a criterion of a minimum total current value of 20 fA when performing calculations and fitting for synthetic M<sup>2</sup>AS data is implemented. Data in which the total current signal is less than this is not used. This work assumes that data is taken as a step-scan such that 5 s of data (*i.e.* concentration, current and electrical mobility) are taken per CPMA classification set-point.

### 6.4.3 Perturbation Analysis

A perturbation analysis was undertaken to assess the sensitivity of the proposed methods in determining particle mass distributions for scenarios in which the charge distribution and morphological parameters of the sampled aerosol are varied.

In this analysis,  $\sigma_{m|d}$  remained fixed at 1.3, as this is close to the average for a range of different soot aerosols [202]. Furthermore, the trends highlighted in the resulting discussion are equally valid for any  $\sigma_{m|d}$  value. Three parameters have been perturbed when calculating the forward model: the values of  $\rho_{\text{eff},100}$ ,  $D_m$  and  $n_{it}$ . Perturbations in  $\rho_{\text{eff},100}$  and  $D_m$

represent changes in the morphology of the aerosol, which can vary between different aerosol sources [147].  $\rho_{\text{eff},100}$  was allowed to vary by  $\pm 30\%$  from a value of  $510 \text{ kg m}^{-3}$  and  $D_m$  by  $\pm 15\%$  from a value of 2.48. These reference values were chosen based on the universal soot relation Olfert and Rogak [147].

Perturbations in  $n_{it}$  can be thought of as mimicking changes in how the sampled aerosol charges. Decreases in charge may occur in experiments due to charger degradation, whilst the acquisition of more charge than predicted may be due to the non-spherical morphology of particles [85, 153, 176]. Rather than illustrate this as changes in  $n_{it}$ , the perturbation in charge is described by a change in the mean charge over the aerosol population from 30 nm to 3000 nm due to a change in  $n_{it}$ . The  $n_{it}$  was perturbed from a value of  $1 \times 10^{14} \text{ s m}^{-3}$  to values of  $5 \times 10^{13} \text{ s m}^{-3}$ ,  $7.5 \times 10^{13} \text{ s m}^{-3}$ ,  $2 \times 10^{14} \text{ s m}^{-3}$  and  $4 \times 10^{14} \text{ s m}^{-3}$ . These changes in  $n_{it}$  equate to corresponding changes in the average mean charge over the entire aerosol population of -11.3%, -4.9%, +11.0% and +21.9%. The perturbation analysis is similar to the framework used by Sipkens et al. [180], but rather than investigating the average transmitted mass, the full mass distribution is of interest.

## 6.5 Results and Discussion

### 6.5.1 Use of a single-valued mass-mobility relation for determining mass distribution sampled from a two-dimensional mass-mobility distribution

As previously discussed, to evaluate the kernel (Eq. 6.01), it is a requirement to assume that the mass-mobility relation is single-valued, an assumption that is not strictly true for a soot-based aerosol in which a distribution of morphologies can exist at a given particle size/mass (see Figure 6.3). For the UDAC-CPMA-CPC system, values of  $\rho_{\text{eff},100} = 510 \text{ kg m}^{-3}$  and  $D_m = 2.48$ , parameters equal to the geometric mean effective density relation of the underlying distribution, are taken. This relation is shown as a black dashed line in Figure 6.4a.

Figure 6.4b shows that using the geometric mean mass–mobility relation to generate the kernel introduces small changes in the inverted size distribution, with discrepancies increasing somewhat as the conditional mass distribution broadens. However, when directly compared to Figure 6.4c, wherein the M<sup>2</sup>AS measures effective density, the differences in the resulting mass distributions are relatively minor. This suggests that, in practice, the choice of effective density used in the kernel has only a limited influence on the overall inversion outcome.

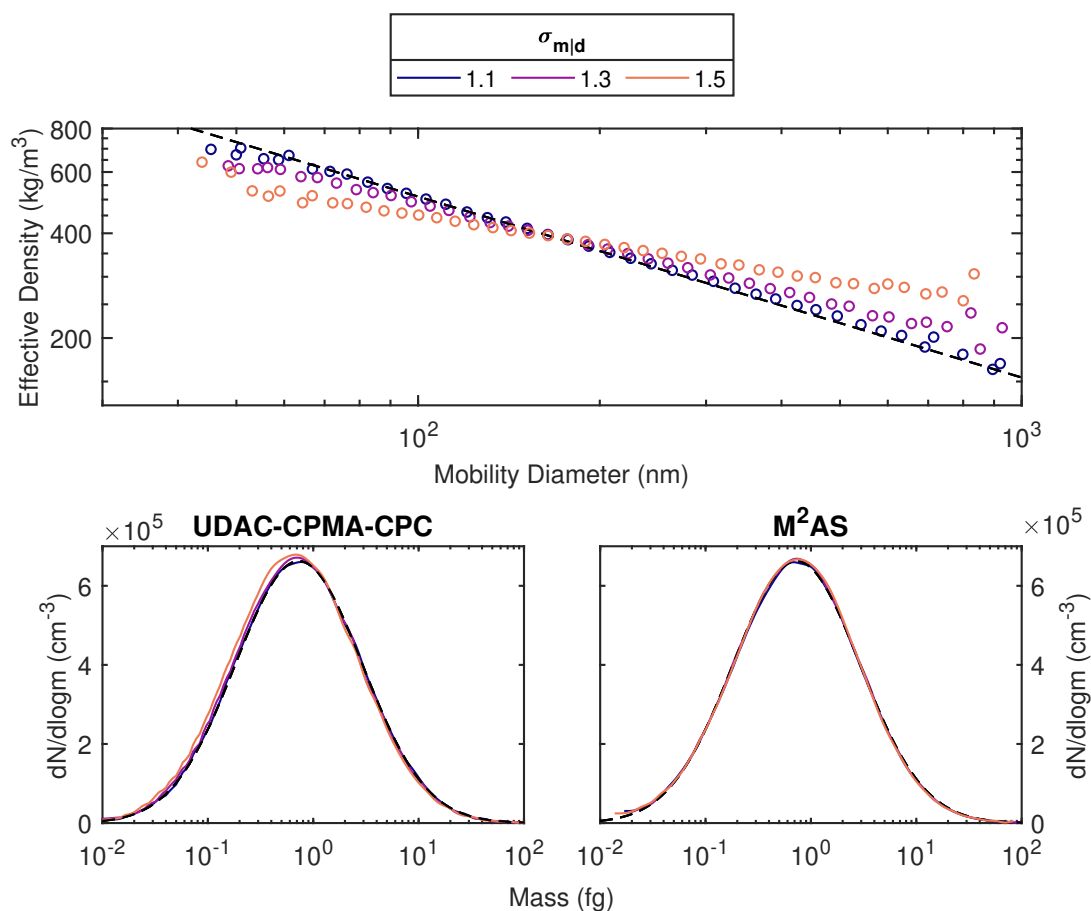


Fig. 6.4 Figure (a) compares the M<sup>2</sup>AS measurements of effective density (scatter markers) to the underlying geometric mean effective density relationship (black dashed line). The measurements have been corrupted with noise as per Section 6.4.2. Mass distributions determined using a UDAC-CPMA-CPC system (b) and M<sup>2</sup>AS (c) are shown for different widths of the conditional mass distribution. The black dashed line in Figures (b) and (c) indicates the true mass distribution.

The M<sup>2</sup>AS measurement returns the average effective density of the CPMA-classified aerosol population (Figure 6.4a), which does not necessarily match the geometric mean of the full two-dimensional distribution due to skewing effects arising from interactions between the kernel and the underlying aerosol distribution, as discussed in Chapter 5. As a result,  $\rho_{\text{eff},100}$  and  $D_m$  obtained from fitting may differ from their 'true' distribution values. Nonetheless, the comparison of Figures 6.4b and 6.4c shows that these differences have a limited impact on the reconstructed mass distribution, and thus the use of a single-valued mass-mobility relation is appropriate.

### 6.5.2 Perturbing Input Conditions: UDAC-CPMA-CPC System

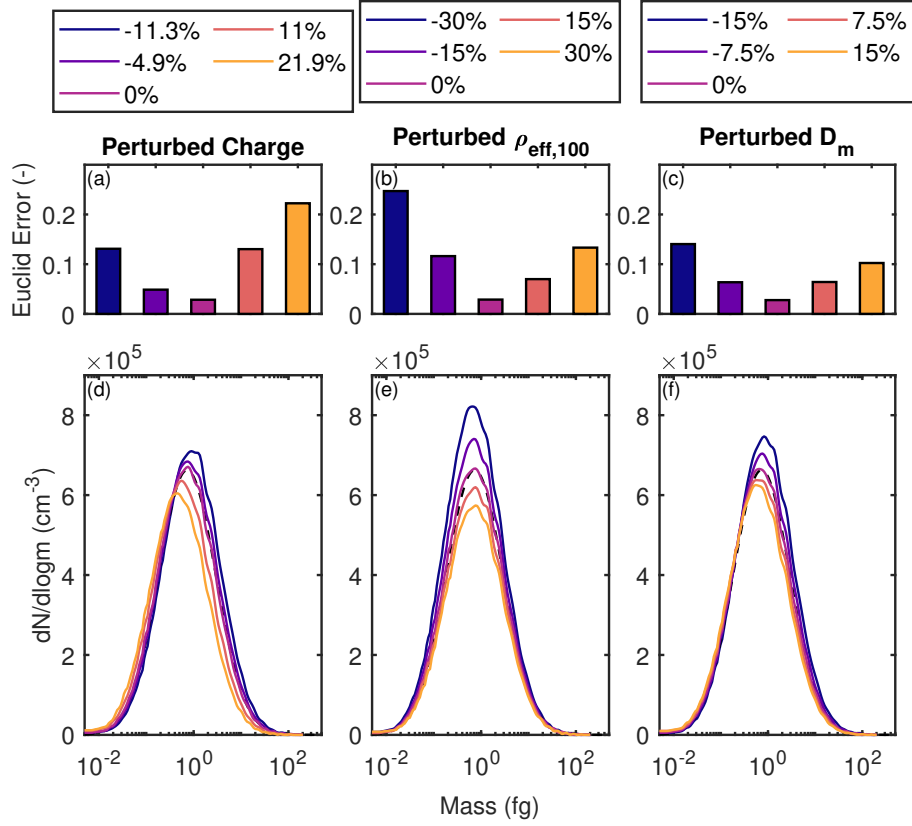


Fig. 6.5 Effect of perturbing parameters on determining the mass distribution using a UDAC-CPMA-CPC set-up. The top panels indicate the Euclidean Error between the inverted distribution and the true distributions, and the bottom panels show the inverted distribution. The system kernel for the Unipolar-CPMA system was determined assuming that the charge distributions follow one in which the  $n_{it}$  is  $1 \times 10^{14} \text{ s m}^{-3}$ , and the effective density follows the universal soot relation e.g.  $\rho_{\text{eff},100} = 510 \text{ kg m}^{-3}$  and  $D_m$  equal to 2.48. From left to right, the effect of perturbing the charge, density pre-factor and density exponent is demonstrated. The percentage error in the corresponding quantity is shown in the legend above each Figure.

The effect of perturbation in the sampled distribution quantities on inverted mass distributions using a UDAC-CPMA-CPC system is shown in Figure 6.5. These results represent the scenario where the assumed parameters to determine the kernel (e.g.  $n_{it} = 1 \times 10^{14} \text{ s m}^{-3}$  and  $\rho_{\text{eff},100} = 510 \text{ kg m}^{-3}$   $D_m = 2.48$  as detailed in section 6.3.1 for the UDAC-CPMA-CPC system) deviate from those of the sampled distribution. Significant errors can be seen as the characteristics of the sampled aerosol are perturbed away from the values used to calculate the kernel used in the data inversion. Figure 6.5d shows the effect of variations in particle charge on the inverted distribution. If particles attain higher charge levels than assumed,

the distribution shifts to the left in mass space as, for a given mass-to-charge ratio, the predicted transmitted mass becomes smaller, following the smaller mean charge predicted by the inversion kernel. Increases of 11% and 21.9% of the average aerosol charge are well within previous experimental measurements of aggregates relative to spheres of the same mobility size [85, 144, 176, 153]. These results demonstrate the sensitivity of this method to uncertainty in the particle charge distribution, which is linked to the morphology of the aerosol. If particles attain a lower charge than predicted, then the distribution shifts in an opposing manner. Undercharging is likely less of an issue in practical applications. However, degradation of charging performance can occur if the charger used gets sufficiently dirty or when using system components that can off-gas, such as conductive silicone tubing [9]. It can also be challenging to accurately determine the exact operating  $n/t$  value, depending on the charger design [175], which adds further uncertainty to the charger's performance.

The effect of changing the mass–mobility parameters is shown in Figures 6.5e and 6.5f. When the density prefactor is varied, a largely uniform change is observed in the amplitude of the reconstructed mass distributions, with only minor shifts in the modal mass. Specifically, when the true value of  $\rho_{\text{eff},100}$  is higher than the value assumed in the inversion, the concentration is systematically underestimated; conversely, when it is lower, the concentration is overestimated. In contrast, perturbations to the exponent  $D_m$  result in a more pronounced shift in the mode of the distribution, with relatively little effect on the overall concentration. These differing behaviours can be explained by the formulation of the effective density relation used in this work (Equation 6.05) and by considering how the forward model is evaluated.

The forward model inversion kernel (Equation 6.01) is constructed on a fixed two-dimensional grid of mass and mobility diameter, and this grid remains unchanged when either  $\rho_{\text{eff},100}$  or  $D_m$  is perturbed. As a result, the charge distribution—evaluated as a function of the mobility diameter at each grid point—remains unchanged, as does the evaluation of the CPMA transfer function. Instead, it is the distribution of concentration at each grid point,  $dn(m, d_m)$ , that is repositioned on the grid prior to convolution with the kernel. Varying  $\rho_{\text{eff},100}$  shifts the entire distribution along the diameter axis, leading to an approximately uniform scaling of the retrieved number concentration. In contrast, adjusting  $D_m$  results in a diameter-dependent transformation: grid cells near the normalisation point of the effective density relation,  $d_m = 100\text{nm}$ , are minimally affected, while those farther from this point are displaced more significantly. When this warped two-dimensional distribution is passed through the fixed kernel, mass- and diameter-dependent biases in the retrieved concentration emerge, rather than a uniform offset.

It should be noted that while this analysis considers variations in each parameter independently, there is likely co-dependence between them in practice. The variability in effective density across different soot sources can be substantial [147, 130], and both  $\rho_{\text{eff},100}$  and  $D_m$  may vary concurrently, introducing additional uncertainty into the mass–mobility relationship.

### 6.5.3 Perturbing Input Conditions: The $M^2AS$

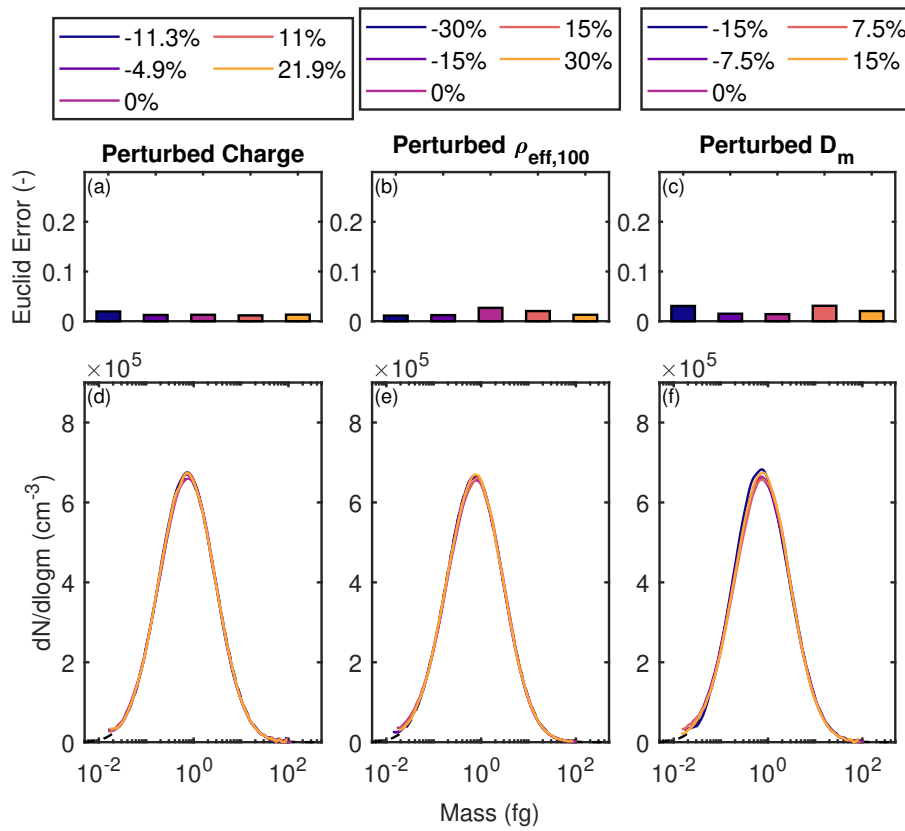


Fig. 6.6 Effect of perturbing parameters on determining the mass distribution using a  $M^2AS$  set-up. The top panels (a), (b) and (c), indicate the Euclidean error, and the bottom panels, (d), (e) and (f), show the inverted distributions. From left to right, the effect of perturbing the charge, density pre-factor and density exponent is demonstrated. The percentage error in the corresponding quantity is shown in the legend above each Figure.

The same perturbation analysis was conducted for the  $M^2AS$ , with the results presented in Figure 6.6. In  $M^2AS$  measurements, both charge and mobility diameter are directly measured, constraining the relationship between mass, mobility diameter, and charge. As a result, there is no reliance on prior assumptions about the mass–mobility relationship or the particle

charge distribution. Due to these additional measurements provided by the MSE, the sampled mass distribution can be accurately reconstructed, as shown by comparing the Euclidean error in Figures 6.6a–c relative to Figures 6.5a–c, regardless of which input conditions are perturbed. This demonstrates that measuring both charge and mobility significantly enhances the accuracy of particle mass distribution determinations in unipolar charger–particle mass analyser systems. Minor discrepancies are consistently observed between the reconstructed and input distributions across different perturbation scenarios. These differences arise from approximating the charge distribution as Gaussian and using fitting techniques to derive model parameters for kernel determination.

#### 6.5.4 $M^2AS$ conversion to mobility and aerodynamic size distributions

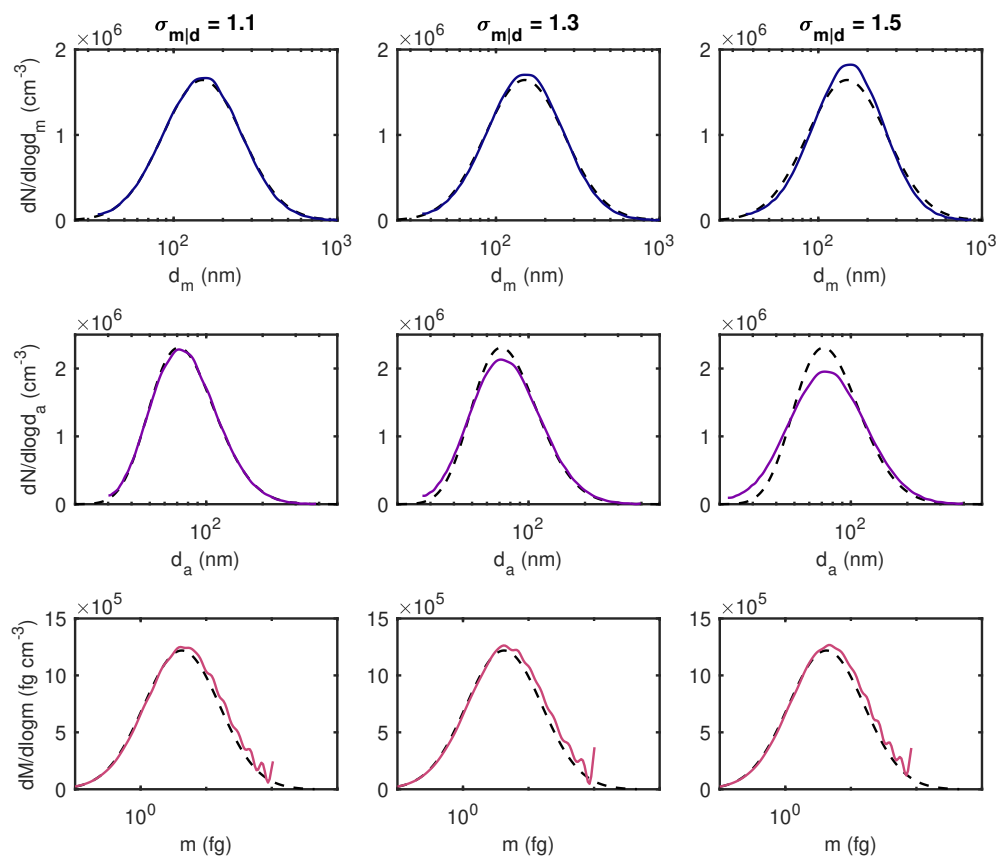


Fig. 6.7 Comparison of number weighted mobility (blue lines, top row), number weighted aerodynamic (red lines, middle row) and mass-weighted mass (purple lines, bottom row) distributions obtained from converting  $M^2AS$  mass distributions using the measured effective density relationship compared to the corresponding underlying distribution (black dashed line) for increasing conditional mass widths (left-to-right).

Since the  $M^2AS$  system measures average effective density, Equations 6.22, 6.23, and 6.24 can be used to convert the number-weighted mass distribution into number-weighted mobility and aerodynamic distributions, as well as a mass-weighted mass distribution, respectively. However, as highlighted by Chapter 5 and reiterated in this work, the  $M^2AS$  strictly measures the average density of the CPMA classified aerosol population. As the width of the two-dimensional distribution increases, this average deviates further from the geometric mean density of the entire population.

Although the mass distribution can be accurately determined, conversions to other particle property domains become increasingly error-prone, with errors growing as particle morphology becomes more variable. This is illustrated in Figure 6.7, which shows the determined mobility distribution (top row) and aerodynamic distribution (middle row) for increasing conditional mass widths. When the conditional width is close to unity (*i.e.*, particles are more compact), conversion errors between different property spaces remain small. However, as the width increases (*i.e.*, morphology becomes more varied), discrepancies between the determined and true distributions become more pronounced.

This suggests that experimental measurements of mobility and aerodynamic distributions for soot and other non-spherical aerosols may deviate from the 'true' underlying distribution. Notably, the mass-weighted mass distribution (bottom panel of Figure 6.7) remains unaffected, as its conversion does not depend on effective density (Equation 6.24).

### 6.5.5 Practical Limitations of the $M^2AS$

While measuring charge and mobility significantly enhances the accuracy of mass distribution determination, the  $M^2AS$  system has two key instrumentation limitations that should be addressed.

The first limitation concerns the quality of data obtained from the MSE, which enables particle charge and electrical mobility measurements. The accuracy of these measurements is highly sensitive to the electrometer signal. A poor signal-to-noise ratio in the electrometers affects both the measurement of average charge and the MSE's ability to balance its electrometer outputs, thereby constraining the size range over which distributions can be measured. This is illustrated in Figure 6.8, which illustrates the total electrometer current (*i.e.*  $i_h + i_l$ ) as a function of the total aerosol concentration. It should be noted that this relationship is illustrative only, as the total current also depends on the aerosol size distribution and the  $n_{it}$  is operated.

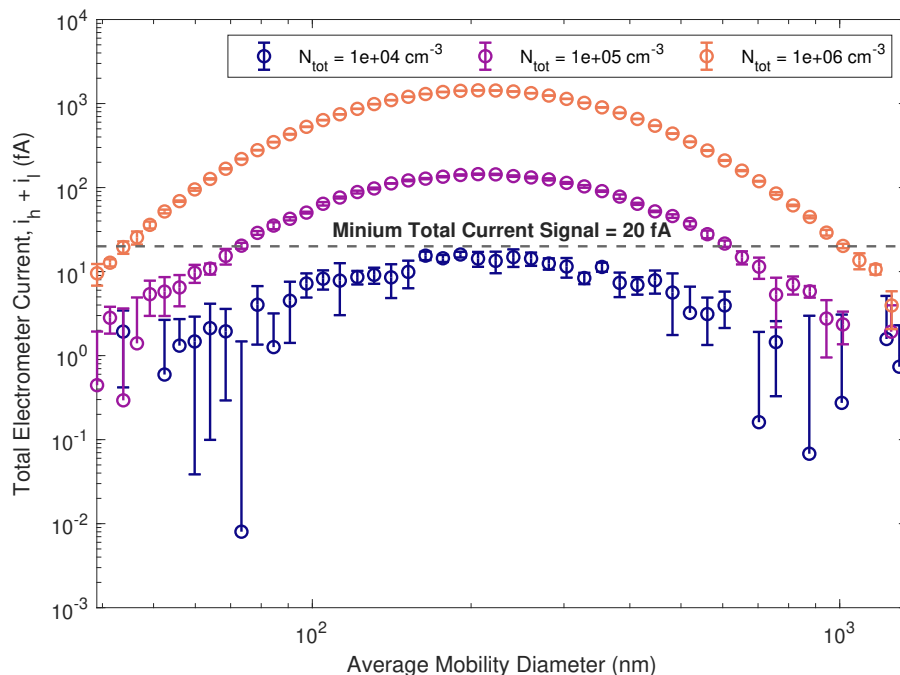


Fig. 6.8 The simulated total current downstream of the CPMA as a function of the average mobility diameter in an M<sup>2</sup>AS system for  $n_{it} = 1 \times 10^{14} \text{ s m}^{-3}$ ,  $D_m = 2.48$  and  $\rho_{\text{eff},100} = 510 \text{ kg m}^{-3}$ . Three total aerosol concentrations are shown, representing the total aerosol concentrations in the upstream sampled distribution. Error bars indicate one standard deviation in the generated synthetic data of the total current signal. A threshold line indicating a current of 20 fA is shown, which is the approximate minimum signal required to obtain measurements with the MSE that are not adversely affected by noise.

Since the electrometer signal scales linearly with number concentration<sup>4</sup>, distributions with lower total number concentrations will have a limited measurement range. Based on a minimum total electrometer signal criterion of 20 fA, no measurements can be taken at a total aerosol concentration of  $1 \times 10^4 \text{ cm}^{-3}$ . As concentration increases, a broader range of measurements becomes possible; however, the full width of the particle size distribution remains unresolved. At total concentrations of  $1 \times 10^5 \text{ cm}^{-3}$ , the measurable range extends from 76 nm to 622 nm, increasing to 44 nm to 1041 nm at  $1 \times 10^6 \text{ cm}^{-3}$ . The inability to capture distribution tails is a significant challenge for the M<sup>2</sup>AS, particularly for smaller particles, which inherently acquire less charge.

Additionally, the theoretical models used in this study do not account for real-world non-idealities, such as increased particle losses or dilution, which could further reduce

<sup>4</sup>Assuming charging remains unaffected by variations in aerosol concentration, which is generally the case when ion concentration is significantly higher than aerosol concentration.

aerosol concentration and measurement sensitivity [133, 19]. While particle number concentrations in the distribution tails could be measured using CPCs, which can count down to concentrations below  $1\text{ cm}^{-3}$ , this approach would lack corresponding average charge and electrical mobility measurements due to the inadequate electrometer signal. Consequently, it would require extrapolating density and charge fit parameters for the smallest and largest particles, introducing uncertainty into the inversion process. Increasing the aerosol flow rate through the MSE could enhance the electrometer signal; however, this brings us to the second limitation—the constraints imposed by hardware.

The smallest classifiable particle mass is limited by the maximum classification speed of the CPMA, which is  $1250\text{ rad s}^{-1}$  for the commercial Cambustion CPMA. To maintain the same mass resolution while increasing flow rate, the CPMA's rotational speed must also increase. Thus, the maximum operational flow rate of the MSE is constrained by the desired mass resolution and particle size range of interest.

## 6.6 Considerations for the numerical study

A few additional notes should be made regarding the formulation of this numerical study. All analyses presented here have been conducted for single-source, unimodal aerosols. The ability to resolve bimodal aerosols, composed of particles with different compositions, is beyond the scope of this work. The  $M^2AS$  may struggle to accurately invert externally mixed aerosols (*e.g.*, soot and salt), where particles with widely varying densities exist at a given mass. In such cases, the concept of an average property becomes less well-defined when a broad range of particles is present. Future investigations—both modelling and experimental—could explore this further.

Additionally, this analysis assumes that charge distribution depends only on mobility diameter, a simplification that aids modelling but may not strictly hold [58]. Charging dynamics for aggregate structures are complex and influenced by factors such as particle capacitance and surface area [176]. For soot aerosols, there is likely a three-dimensional relationship between charge, mobility, and mass, further complicating data inversion. Future work could explore whether this has additional implications for measurement accuracy.

## 6.7 Conclusions

The simulations provided in this work have demonstrated that the sampled mass distribution using a unipolar-CPMA-CPC system can be accurately determined only if the particle's charging behaviour and mass-mobility relation are accurately known. Therefore, mass

distributions determined using a Unipolar Charger - CPMA system may be in error due to the uncertainty of the relation of charging, mass and mobility. This is likely particularly true for non-spherical particles, whose mass-mobility relation and particle charge may vary considerably from assumed models. To resolve this, a new measurement technique has been introduced, the Mass Mobility Aerosol Spectrometer ( $M^2AS$ ), which can theoretically overcome these issues with the additional measurement of charge and mobility enabled by parallel sampling between the MSE and CPC downstream of the CPMA. It has been shown numerically that perturbations in input parameters have minimal effect on the inverted particle mass distribution. However, there are three main limitations to the  $M^2AS$ . Due to the requirement of a current measurement, the  $M^2AS$  can only resolve particle distributions if sufficient concentration is available; this also means the tails of distributions are not well resolved. In addition, smaller particles may not be measured due to hardware limitations of the rotational speed of the CPMA. Finally, if an aerosol with a wide range of morphologies at a given particle mass/size is sampled, mobility and aerodynamic distributions converted from particle mass distributions are more likely to incur error.

Despite these limitations, the  $M^2AS$  offers significant potential benefits: it enables direct, model-independent inference of particle mass distributions, improves measurement fidelity for complex aerosols, and allows for more accurate characterisation of non-spherical or multiply charged particles. This makes the  $M^2AS$  a promising tool for advanced aerosol research. For example, it could be used to investigate combustion-generated aerosols with irregular morphology, assess engineered nanomaterials where assumptions of sphericity and single charging fail. The  $M^2AS$  also offers the potential for more in-depth studies on the fundamental relationships between mass-mobility and charge.

# Chapter 7

## Experimental Evaluation of the Mass Mobility Aerosol Spectrometer (M<sup>2</sup>AS) <sup>1</sup>

### 7.1 Introduction

The M<sup>2</sup>AS system, introduced in Chapter 6, theoretically offers a robust and comprehensive approach for determining particle mass distributions by simultaneously measuring mass, mobility, and charge through the addition of the MSE discussed in Chapter 5. This capability is particularly valuable for characterising aerosols, enabling a detailed understanding of their physical properties. However, although the theoretical models underpinning this system were developed in Chapters 5 and 6, experimental validation is necessary to confirm their accuracy and reliability in practical applications.

This chapter focuses on validating density measurements and particle size distributions obtained using the M<sup>2</sup>AS system through experimental methods. Specifically, it evaluates two categories of aerosols: compact particles with densities close to/equal to their material density and highly fractal soot aerosols, which exhibit lower effective densities due to their complex structures. The accuracy of density measurements is assessed by comparing M<sup>2</sup>AS results with those obtained using a CPMA coupled with an SMPS, a well-established method for determining particle effective density.

In addition to density validation, this chapter examines the accuracy of particle size distributions measured using the M<sup>2</sup>AS system. These distributions are validated by directly comparing data acquired from an SMPS and a CPC. By conducting parallel measurements across multiple aerosol types, this study aims to establish the reliability of the M<sup>2</sup>AS system for determining both particle density and size distributions.

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<sup>1</sup>This chapter is currently being prepared for submission as a manuscript.

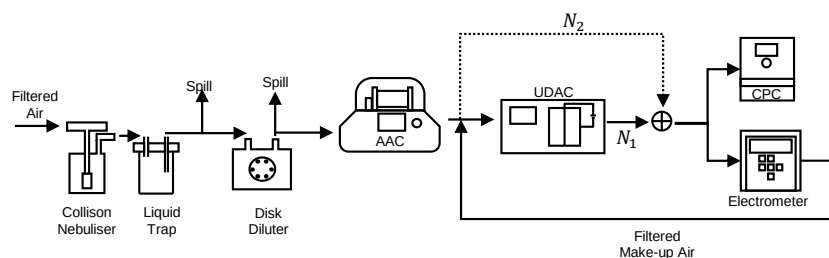


Fig. 7.1 Experimental set-up to evaluate particle losses in the UDAC

## 7.2 Experimental Methods

### 7.2.1 Particle Losses within the M<sup>2</sup>AS

Particle losses within the Unipolar Diffusion Aerosol Charger used as the charger in the M<sup>2</sup>AS system (UDAC Mk.2, Cambustion Ltd.) were evaluated. The experimental setup is shown in Figure 7.1. The UDAC is a Hewitt-type unipolar diffusion charger [69], previously described in detail by Biskos et al. [20]. The version used in this study includes a new 'low-flow core' designed for use with lower aerosol flow rates, optimising its performance for the intended aerosol flow rate of approximately  $1 \text{ L min}^{-1}$  in the M<sup>2</sup>AS system. The charger core consists of a fine wire surrounded by a grounded grid with an outer diameter of 2 cm. An AC square wave voltage of 400 V draws ions through the grounded grid into the aerosol-laden flow. To prevent contamination, a clean inner sheath air flow of  $1.1 \text{ L min}^{-1}$  protects the corona wire, while an outer sheath flow of  $0.6 \text{ L min}^{-1}$  protects the walls. These sheath flows dilute the aerosol sample, resulting in a dilution factor,  $DR$ , of approximately 2.7 when the UDAC operates at an aerosol flow rate of  $1 \text{ L min}^{-1}$ . The UDAC was operated at a nominal ion-concentration time product,  $n_i t$ , set-point of  $4 \times 10^{13} \text{ s m}^{-3}$ , which was determined through calibration with a 250 nm spherical aerosol.

To evaluate particle losses within the UDAC, di-octyl sebacate (DOS) particles and ammonium sulphate particles were generated using a Collison nebuliser. Ammonium sulphate particles were dried using a silica desiccant-filled diffusion dryer to investigate losses at smaller sizes where diffusion dominates. In contrast, DOS particles were used to study losses at larger sizes where inertia dominates. Particle losses were determined by size-selecting particles with an AAC (Cambustion Ltd., UK) operating at a resolution (sheath to aerosol flow rate) of 10. For smaller particle sizes, make-up air was added from the electrometer's exhaust (HEPA filtered) to maintain the required resolution. Consequently, ammonium sulphate measurements were conducted with an aerosol flow rate of  $0.3 \text{ L min}^{-1}$  through the

AAC, while DOS measurements were conducted at  $1 \text{ L min}^{-1}$ . Particle concentrations were measured using a CPC (Model 3752, TSI Inc.) operating at  $0.3 \text{ L min}^{-1}$ . An electrometer pulled an additional  $0.7 \text{ L min}^{-1}$  through the UDAC, maintaining a total aerosol flow rate of approximately  $1 \text{ L min}^{-1}$  through the UDAC. The current measured by the electrometer was not used in subsequent analysis. The concentration downstream of the UDAC (denoted  $N_1$  in Figure 7.1) was measured over 1 minute and averaged. The total concentration upstream of the UDAC ( $N_2$ ) was then measured similarly. The penetration was calculated using the ratio of  $N_1$  to  $N_2$ , adjusted by the dilution factor:

$$P = \frac{N_1}{N_2} \times DR. \quad (7.01)$$

### 7.2.2 Effective density, integrated number and size distribution validation

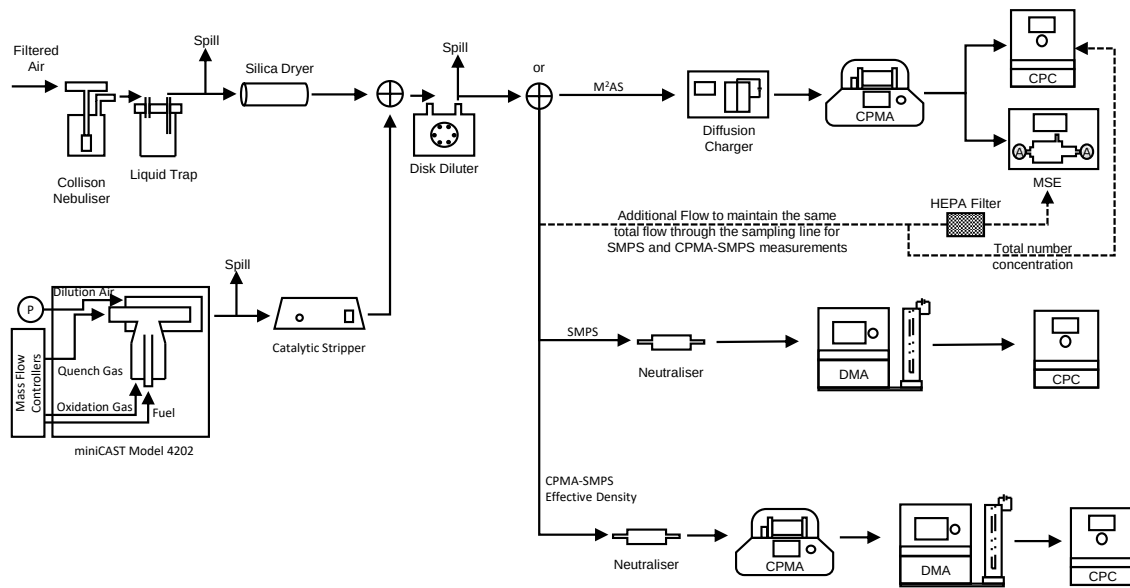


Fig. 7.2 Experimental set-up for validation of the  $M^2AS$ .

The experimental setup used to validate the effective density and distribution measurements of the  $M^2AS$  system is shown in Figure 7.2. The validation was conducted for two categories of aerosols: spherical or compact particles and non-spherical particles. This approach allows for a comprehensive evaluation of the  $M^2AS$  system across a range of particle morphologies. The  $M^2AS$  system in this work consists of a UDAC, which was operated at a nominal ion-concentration time product,  $n_i t$ , set-point of  $4 \times 10^{13} \text{ s m}^{-3}$  a CPMA (Model

Mk2, Cambustion Ltd. UK) and then parallel measurement by the combination of a CPC and MSE. The model of CPC was changed depending on the validation being performed, as discussed below.

For spherical or compact particles, polydisperse aerosols were generated by nebulising solutions using a Collison nebuliser. A liquid trap placed downstream of the nebuliser was used to remove larger droplets. Optionally, a silica dryer was employed to dry the aerosol. The resulting flow was then diluted using a disk diluter.

Two aerosol types were investigated: ammonium sulphate and DOS. DOS produces spherical droplets with a well-defined density of  $913 \text{ kg m}^{-3}$ , whereas ammonium sulphate typically forms compact particles with a density close to its bulk value of  $1770 \text{ kg m}^{-3}$  [224]. DOS is particularly useful for validating effective density measurements due to its uniform spherical morphology. Density measurements obtained from the M<sup>2</sup>AS were validated using three different CPC models: a TSI 3752, a TSI 3790, and a Brechtel 1720 mixing-type CPC.

In addition to density validation, inverted M<sup>2</sup>AS mobility distributions of ammonium Sulphate and DOS were compared with mobility size distributions measured using a SMPS. The distribution validation was performed separately from the density validation measurement; in these measurements, validation was only performed using a TSI 3752 CPC as the particle counter in the M<sup>2</sup>AS. The SMPS system for distribution validation consisted of a bipolar charger (Model 3077A, TSI Inc., USA), a DMA (Model 3082, TSI Inc., USA), and a 3752 TSI CPC in series. The SMPS was operated with an aerosol flow rate of  $0.3 \text{ L min}^{-1}$  and a sheath flow of  $3 \text{ L min}^{-1}$ , with each scan lasting three minutes. For all measurements, the M<sup>2</sup>AS was operated in stepped mode. In this mode, the CPMA mass-to-charge set-point was incremented and stabilised before measurement. At each set-point, the CPC recorded the number concentration, while the MSE measured the current and average electrical mobility over 10 s, averaging the results. The CPMA was operated at an  $R_{m,q}$  of 3 for all measurements, as defined in Chapter 4. Due to equipment availability, SMPS and M<sup>2</sup>AS measurements were performed sequentially rather than in parallel. To maintain consistent sampling conditions, additional flow was pulled using the MSE, ensuring that the total flow rate during SMPS measurements was the same as during M<sup>2</sup>AS measurements. The total concentration was measured by bypassing the relevant equipment and sampling directly with the CPC. The dilution ratio of the disk diluter was increased to ensure that the CPC operated in single-count mode when measuring the total concentration.

For non-spherical particle validation, soot was generated using two different sources. The first was a miniCAST (Model No. 4202), where the density and size of the soot were adjusted by varying the flow rates of the fuel, oxidation gas, and dilution air. Three operating

conditions were used to produce different aerosol size distributions, hereafter referred to as CAST settings 1, 2, and 3.

For these settings, the oxidation gas (air) flow rates were  $1.85 \text{ L min}^{-1}$ ,  $1.36 \text{ L min}^{-1}$ , and  $1.5 \text{ L min}^{-1}$ , respectively. The fuel flow rate was  $0.07 \text{ L min}^{-1}$  for setting 1 and  $0.06 \text{ L min}^{-1}$  for settings 2 and 3. The quench gas (nitrogen) flow was set to  $6.5 \text{ L min}^{-1}$  for settings 1 and 2, and  $7.5 \text{ L min}^{-1}$  for setting 3. The dilution flow was regulated using a pressure controller set to 0.5, 2, and 3 bar gauge pressure for settings 1, 2, and 3, respectively.

In addition to miniCAST particles, soot aerosol was also generated using a Cambustion Diesel Particle Generator (DPG). After generation, all generated soot particles were passed through a catalytic stripper to remove any semi-volatile components.

To validate the  $M^2AS$  density measurement for non-spherical particles, an additional measurement was conducted using a CPMA and SMPS in tandem to determine the average effective density. This setup is illustrated in the lower path of Figure 7.2. Particles were first charged using a bipolar charger and then mass-selected using the CPMA, which was operated at a single-charge mass resolution of  $R_m = 5$ , as defined by Reavell et al. [162]. The average particle mobility diameter was determined by fitting a Gaussian distribution to the mobility distribution of the mass-selected particles. The mean of the Gaussian fit to the mobility data  $\overline{d_m}$ , along with the CPMA's mass-to-charge set-point (assuming singly charged particles ( $s^* = m^*$ )), was then used in the equation  $6m^*/\pi\overline{d_m}^3$  to calculate the effective density. Mobility distribution and total concentration measurements were performed in the same manner as for the spherical particle validation. No total concentration measurements were taken for CAST Settings 1 and 2. However, the integrated concentration can be compared to the integrated concentration of the SMPS distribution, which has an accuracy of  $\pm 30\%$  for soot aerosols [53, 123].

In addition to the average effective density obtained through Gaussian fitting methods. The CPMA-SMPS system can obtain two-dimensional mass-mobility data through inversion techniques [178, 161, 180]. Here, a two-dimensional mass-mobility distribution is obtained from the inversion of CPMA-SMPS data for the Cast setting 3 soot. The data was inverted using the methods and code described by Sipkens et al. [178]. This provides a measure of the diversity in particle morphology and also marginal mass and mobility distributions, which can be readily compared to distributions obtained by the  $M^2AS$ .

For all  $M^2AS$  distribution measurements, both for compact and non-spherical aerosols, validation was performed by comparing the lognormal distribution parameters fitted to the size distributions determined by the  $M^2AS$  with lognormal distribution parameters obtained from fitting to the SMPS mobility distribution. The inversion method used to derive the particle mass distribution followed the approach described in Chapter 6, including the

fitting of the average charge and average mass-mobility data. However, two key differences exist between the methods used in Chapter 6 and those applied in this experimental work. Firstly, rather than using the analytical form of the CPMA transfer function described by [182], a Monte Carlo simulation was implemented to determine the CPMA transfer function. Secondly, experimental systems often exhibit non-idealities relative to theoretical models, leading to particle losses that must be accounted for. Both of these differences are discussed in detail in Section 7.3.

Since the inversion of M<sup>2</sup>AS data returns a mass distribution, it was necessary to convert this into a mobility diameter distribution to compare with SMPS measurements. This was done by determining the mass-mobility exponent ( $D_m$ ) and reference density ( $\rho_{\text{eff},100}$ ) through fitting (as detailed in Chapter 6) and then applying the following equation to relate the mobility diameter to mass:

$$m = \frac{\pi}{6} \rho_{\text{eff},100} d_{m,100}^{3-D_m} d_m^{D_m} \quad (7.02)$$

where  $m$  is the particle mass,  $d_m$  is the mobility diameter,  $d_{m,100}$  is the reference mobility diameter of 100 nm. The concentration in each size bin was then divided by the bin width in mobility log-space to obtain the lognormal mobility distribution,  $dN/d \log d_m$ . Values of  $\rho_{\text{eff},100}$  reported in the results are abbreviated to  $\rho_{100}$  to improve the readability of Figures and Tables.

### 7.2.3 M<sup>2</sup>AS Calibration Procedure

Calibration before measurement is critical to obtaining accurate data from the M<sup>2</sup>AS. The current calibration method extensively uses a DMA, beginning with its calibration. This process follows the procedures outlined by Wiedensohler et al. [220] and Wiedensohler et al. [219]. The sheath flow rate and voltage of the DMA are calibrated using a Gilibrator and voltmeter, respectively. Subsequently, an SMPS scan is performed for  $221 \text{ nm} \pm 6 \text{ nm}$  PSL particles, with a scan time of 3 minutes. A Gaussian fit applied to the +1 charge peak yielded a mean diameter of 224.5 nm, corresponding to an error of 1.4%. This is well within the recommended uncertainty of 3.5%, as specified by [219], which includes a 2.7% uncertainty in PSL size and 1-2% uncertainty in sheath flow rate.

The CPMA used in the M<sup>2</sup>AS measurements was calibrated using DOS particles selected by the DMA. To match the calibration size of the PSL particles, DOS particles with a mobility diameter of 220 nm were classified using the DMA and subsequently used for CPMA calibration. DOS was chosen as its concentration remained more stable over the duration of a CPMA step scan (approximately 20 minutes) compared to PSL particles. It

was found that the peak single-charge mass measured by the CPMA was within 1.6% of the DMA diameter set-point. The DMA was also used to calibrate the effective length of the MSE, as detailed in Chapter 5.

The final calibration step is the single-charge calibration, which is essential for obtaining an accurate charge measurement. This calibration determines the ratio of counting efficiency between the CPC and the electrometer. It is performed by generating a population of singly charged particles using a tandem CPMA-DMA. By overlapping the transfer functions of the two classifiers, it is ensured that only singly charged particles exit the second classifier [184]. The single-point charge calibration is conducted by selecting 150 nm particles, with both the DMA and CPMA operating at resolutions of 10 and 5 in mobility and mass space, respectively. The singly charged particles are sampled in parallel with the CPC and MSE, allowing the determination of the calibration coefficient to account for counting efficiency discrepancies between the CPC and MSE.

For the MSE sample flow rate used in this work (0.7 L min<sup>-1</sup>), a particle concentration of  $4 \times 10^4 \text{ cm}^{-3}$  corresponds to approximately 37 fA in each electrometer. This makes the single-charge calibration sensitive to electrometer zero offsets and noise. It is important to note that a single-point charge calibration implicitly assumes the linearity of both the electrometer and the CPC, which is a reasonable assumption for most CPCs operating in their single-counting mode. Additionally, this assumption relies on the counting efficiency being independent of particle size, which is typically valid between 50 nm and 1  $\mu\text{m}$  for most CPC types. However, roll-off (i.e., reduced counting efficiency) may occur at smaller or larger particle sizes due to growth kinetics [212, 55] and inertial losses [168, 201], respectively.

## 7.3 Inversion of M<sup>2</sup>AS measurements

### 7.3.1 Calculation of the CPMA Transfer Function

The inversion of M<sup>2</sup>AS measurements is performed in the same manner as Chapter 6. However, there are two notable differences in the calculation of the transfer function of the CPMA. The concentration at the  $i^{\text{th}}$  measurement point is given by

$$N_i = \int K_i(m) \frac{dN}{d\log m} d\log m + \varepsilon_i. \quad (7.03)$$

where  $\frac{dN}{d\log m}$  is the lognormal mass distribution function and  $\varepsilon_i$  is the error in the  $i^{\text{th}}$  CPC concentration measurement.  $K_i(m)$  is the system kernel which is a function of the particle charge distribution and the CPMA transfer function, as discussed in detail in Chapter 6. To determine the CPMA transfer function, the analytical approach developed by Sipkens et al.

[182] could be used, as implemented in Chapters 5 and 6. However, for M<sup>2</sup>AS measurements, a Monte Carlo particle tracking method is opted for, detailed in Appendix D. This choice is motivated by the need for compatibility with future research, where the CPMA's speed and voltage will be dynamically varied (scanned) over time to reduce measurement duration and increase the number of measurement classes per decade. Unlike the analytical methods of Sipkens et al. [182], the Monte Carlo approach can be readily extended to accommodate time-varying operational conditions. However, it is important to note that for the measurements conducted in this study, the CPMA was operated using a stepped profile. Under these conditions, the transfer function computed via Monte Carlo simulation is essentially identical to that obtained analytically, ensuring consistency between the two approaches.<sup>2</sup>

### 7.3.2 Particle Losses within the CPMA

Along with the slight modification in transfer function calculation, non-idealities in the CPMA's transfer function are accounted for. The Monte Carlo-derived transfer function, as well as all other theoretically derived transfer functions, strictly pertain to the classification region of the CPMA. However, in practice, the overall transfer function of the device may deviate from theoretical predictions due to factors such as particle losses at the inlet and exit regions or non-uniformities in the fluid flow profile.

Olfert et al. [146] investigated these non-idealities in a prototype CPMA, finding that transmission efficiency varied with rotational speed. More recently, Naseri et al. [133] experimentally determined the transfer function of the commercial Mk1 CPMA using a tandem CPMA setup, allowing full deconvolution of the data to extract both a height factor and a width factor, which scale the height and width of the theoretical transfer function respectively. Their analysis, based on the triangular form of the CPMA transfer function [162], revealed that while the width factor closely matched theoretical predictions, the height factor exhibited significant discrepancies.

To parameterise their findings, Naseri et al. [133] performed multivariate fitting, yielding complex functions that describe the height and width factors as functions of the single-charge particle mass set-point, aerosol flow rate, and single-charge mass resolution. The width factor can be determined using the following equation:

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<sup>2</sup>Except for diffusion effects, where the analytical method slightly overestimates particle penetration, as discussed in Appendix D.

$$\mu(m^*, R_{m,+1}, Q) = \frac{a_l}{1 + \exp(-b_l \cdot (\log_{10}(m^*)) + c_l)} \quad (7.04)$$

$$a_l = 0.0258Q + 1.31R_{m,+1}^{-2.57} + 1.12 \quad (7.05)$$

$$b_l = 4.07R_m + 0.967, \quad (7.06)$$

$$c_l = 4.63R_m + 0.428 \quad (7.07)$$

where  $m^*$  is the nominal singly charged mass set-point of the CPMA,  $R_{m,+1}$  is the single charge resolution, which can be calculated using the method of Reavell et al. [162] and  $Q$  is the flow rate through the classifier. The height factor for a given aerosol flow can be calculated from

$$h(m^*, R_{m,+1}, Q)|_{Q=\text{const}} = \frac{a_l}{1 + \exp(-b_l \cdot (\log_{10}(m^*)) + c_l)} \quad (7.08)$$

$$a_l = a_1 R_{m,+1}^3 + a_2 R_{m,+1}^2 + a_3 R_{m,+1} + a_4 \quad (7.09)$$

$$b_l = b_2 R_{m,+1} + b_1, \quad (7.10)$$

$$c_l = c_1 \exp(c_2 R_{m,+1}) + c_3. \quad (7.11)$$

where constants  $a, b$  and  $c$  are given in Table 7.1 for flow rates of 0.3 L min<sup>-1</sup> and 1.5 L min<sup>-1</sup>.

Table 7.1 Coefficients for the particle height factor for flow rates of 0.3 L min<sup>-1</sup> and 1.5 L min<sup>-1</sup>

|                  | Coefficients |       |         |       |         |       |         |         |        |
|------------------|--------------|-------|---------|-------|---------|-------|---------|---------|--------|
|                  | $a_1$        | $a_2$ | $a_3$   | $a_4$ | $b_1$   | $b_2$ | $c_1$   | $c_2$   | $c_3$  |
| Q <sub>0.3</sub> | -0.000605    | 0.017 | -0.159  | 1.373 | 0.00970 | 1.49  | -0.0125 | 0.305   | 0.730  |
| Q <sub>1.5</sub> | 0.000        | 0.000 | -0.0130 | 0.950 | 0.151   | 1.89  | 2.37    | -0.0636 | -0.482 |

There are a few things to note before utilising these functions within the inversion process of the M<sup>2</sup>AS. The first is that the nominal mass set-point of the CPMA,  $m^*$ , as used in the above equations, assumes that all particles have a single elementary charge such that the mass-to-charge point of the CPMA,  $s^*$ , is equal to  $m^*$ . This is clearly not the case for the M<sup>2</sup>AS where particles are unipolarly charged; therefore, the average transmitted mass determined by multiplying the mass-to-charge set-point by the measured average charge,  $\bar{m} = s^* \bar{q}$ , is used in place of  $m^*$  in Equations 7.04 and 7.08. Secondly, the resolution of the CPMA for

M<sup>2</sup>AS measurements is defined differently than the single charge, utilising a resolution which incorporates the fact that particles are unipolarly charged as described in Chapter 4. The equivalent single charged resolution,  $R_{m,+1}$ , to select a particle of the transmitted average mass at the operating rotational speed of the classifier, can be determined using the method of Reavell et al. [162]. Finally, Naseri et al. [133] evaluated the transfer function at 0.3 L min<sup>-1</sup> and 1.5 L min<sup>-1</sup>. The flow through the CPMA for M<sup>2</sup>AS measurements was 1 L min<sup>-1</sup> and therefore linear interpolation, as per the suggestion of Naseri et al. [133], is used to determine the loss factor at 1 L min<sup>-1</sup>.

To simplify matters, the width factor has been ignored in the deconvolution presented here, as it was found to be relatively close to theory [133]. The height factor only scales the height, not the area (which is the parameter which determines particle loss). Therefore, the transmission efficiency,  $\lambda$  is defined as  $\lambda = h/\mu$ . Equation 7.03 is therefore modified to include losses through both the UDAC and CPMA and becomes

$$N_i = \int P(m) \lambda(m) K_i(m) \frac{dN}{d\log m} d\log m + \epsilon_i \quad (7.12)$$

where  $P(m)$  is the penetration through the UDAC and  $\lambda(m)$  is the transmission efficiency of particles through the CPMA. A final simplifying assumption is made; both  $P(m)$  and  $\lambda(m)$  are assumed to be constant over the width of the transfer function, such that they can be taken outside the integral

$$N_i = P|_{\bar{m}_i} \lambda|_{\bar{m}_i} \int K_i(m) \frac{dN}{d\log m} d\log m + \epsilon_i. \quad (7.13)$$

where  $|_{\bar{m}_i}$  denotes that the functions  $P$  and  $\lambda$  are evaluated at the average transmitted particle mass. Therefore, the number concentration measured at each CPMA set-point is simply scaled by  $P|_{\bar{m}_i}$  and  $\lambda|_{\bar{m}_i}$  to obtain a corrected concentration.

## 7.4 Results and Discussion

### 7.4.1 Loss characterisation of the UDAC

Figure 7.3 illustrates the particle penetration as a function of particle size through the UDAC. As anticipated, the penetration decreases for both smaller and larger particles due to diffusive and impaction losses, respectively. For particles between 100 nm and 2000 nm, the loss remains relatively constant, though not equal to unity, indicating the presence of electrostatic losses within the charger. These losses likely remain consistent across this size range, as

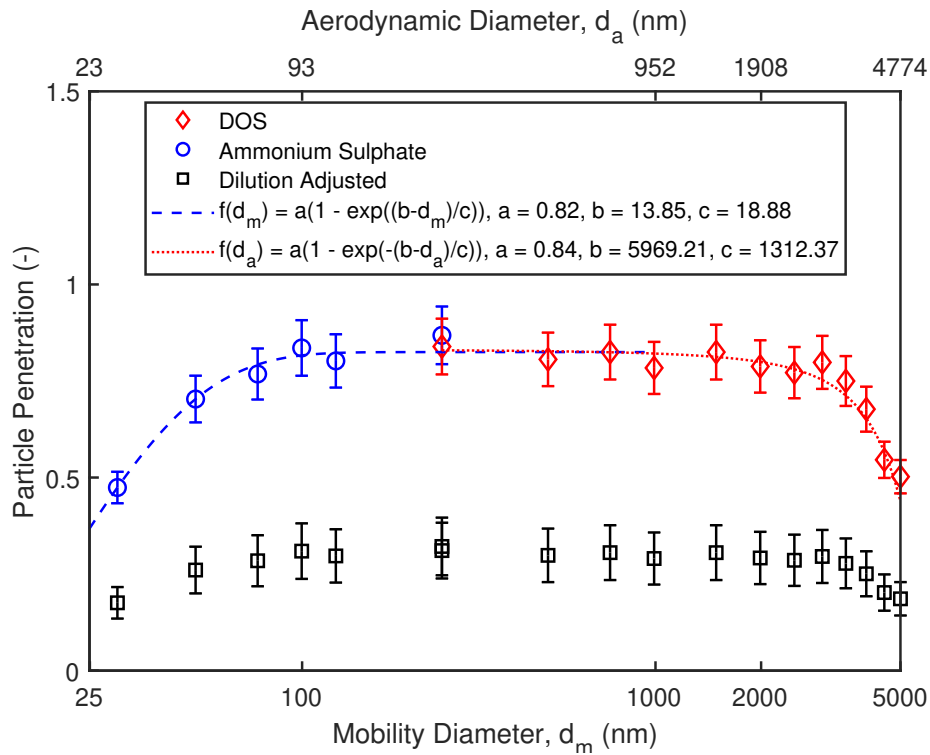


Fig. 7.3 Penetration through the Mk2 UDAC at a flow rate of  $\sim 1 \text{ L min}^{-1}$ . Roll-off functions were fit to the data to model used as a function of diffusion and impaction, respectively. Error bars include Type A and Type B uncertainties. Type A uncertainties are taken as 1 standard deviation in the measurement. Type B uncertainties are taken as 5% in CPC concentration. The aerodynamic diameter on the top axis is determined from the mobility diameter assuming spherical DOS particles with a bulk density of  $913 \text{ kg m}^{-3}$ .

electrostatic losses are a function of electrical mobility, which varies weakly with size for a unipolarly charged aerosol.

Two roll-off functions have been fitted to the data to account for these losses within the UDAC system. Additionally, the effective penetration is shown, incorporating the dilution factor of the UDAC. The Cambustion UDAC used in this study dilutes the incoming aerosol due to the additional sheath flows, which help maintain the cleanliness of the charger, by a factor of approximately 2.7. This dilution introduces a significant effective loss. Optimising this aspect in the future could enable measurements across a wider size range, as the signal-to-noise ratio could potentially improve by nearly a factor of 3.

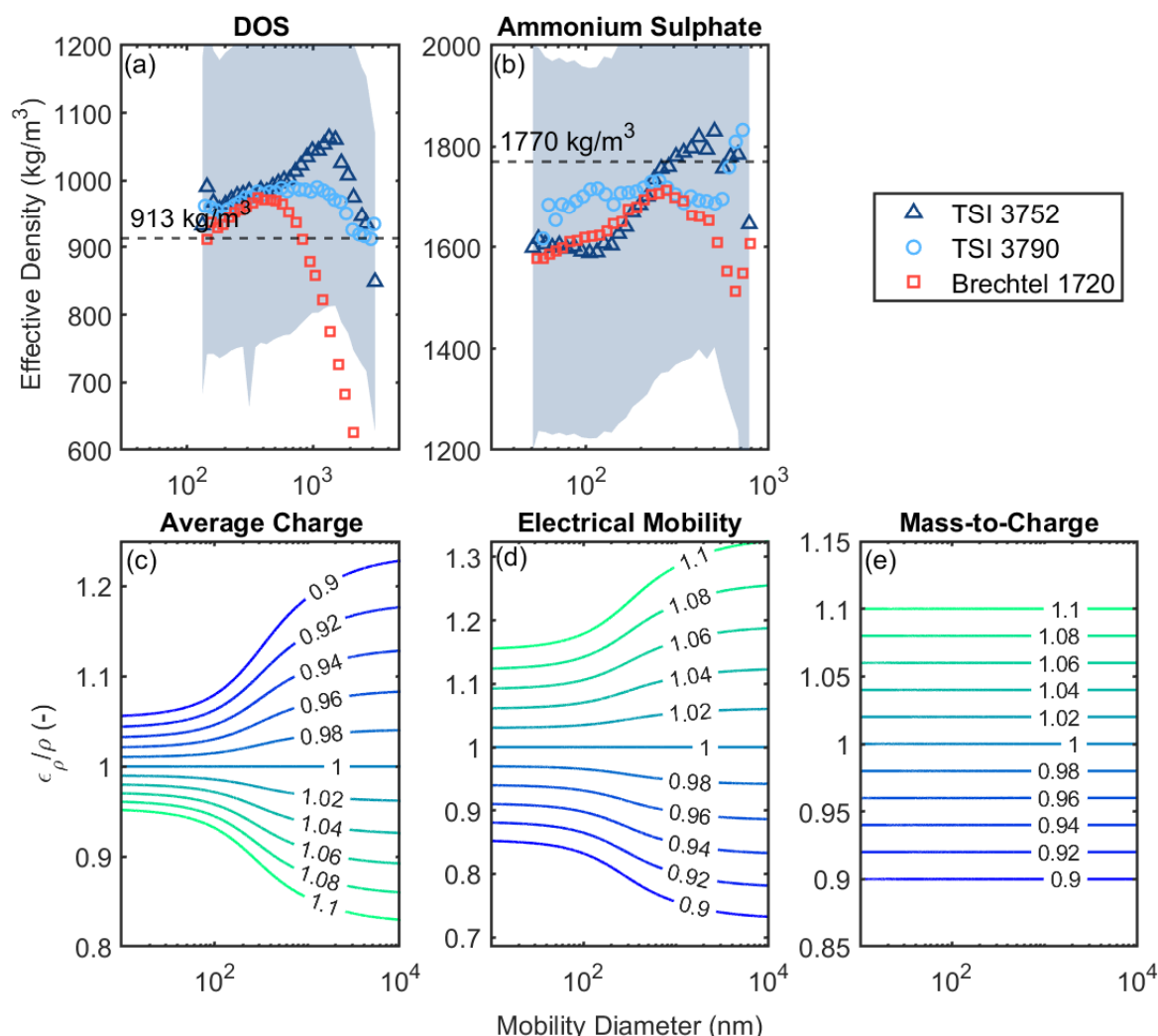


Fig. 7.4 Figures (a) and (b) show the experimentally measured effective density of DOS and ammonium sulphate aerosol, respectively. The black dashed lines in (a) and (b) indicate the bulk density of each material. The shaded area indicates uncertainty in the measurement, including both Type A uncertainties, taken as 1 standard deviation in the mean of the measurement, and Type B uncertainties calculated as detailed in Appendix D.3. Note that only the uncertainty for the TSI 3752 is shown for clarity. The uncertainties for the other two CPCs are of similar magnitude. The bottom row of figures illustrates theoretical errors in effective density as a function of errors in (c) average charge, (d) average electrical mobility and (e) CPMA mass-to-charge ratio.

#### 7.4.2 Validation of Effective Density Measurements using DOS and Ammonium Sulphate

To validate the effective density measurement of the M<sup>2</sup>AS, measurements were made of DOS aerosol, which has a known bulk density of 913  $\text{kg m}^{-3}$ , and ammonium sulphate,

which generally forms compact particles close to its bulk density of  $1770 \text{ kg m}^{-3}$  [224]. This measurement was repeated with different models of CPCs. Figure 7.4 (a) shows the measurement of the effective density of DOS, and Figure 7.4 (b) shows the measurements of ammonium sulphate. The shaded area around the scatter points indicates the uncertainty in the measurement, as described in Appendix D. Only the uncertainty for the measurements taken with the TSI 3752 CPC is shown to improve clarity, as the uncertainties for the other CPCs are similar. Note that the uncertainty of the measurements increases at the tails of the distribution, where the current becomes smaller due to lower concentrations and, in the case of smaller particles, lower charges per particle. For accurate measurements of effective density charge, calibration is paramount. All three CPCs undercounted relative to the MSE when measuring singly charged particles. As such, the CPC concentration measurement had to be multiplied by 1.085, 1.16, and 1.14 for the TSI 3752, Brechtel 1720 mixing CPC, and TSI 3790, respectively.

The average effective density of DOS particles measured by the M<sup>2</sup>AS was  $991 \text{ kg m}^{-3}$  ( $\pm 142 \text{ kg m}^{-3}$ ),  $966 \text{ kg m}^{-3}$  ( $\pm 53 \text{ kg m}^{-3}$ ), and  $780 \text{ kg m}^{-3}$  ( $\pm 714 \text{ kg m}^{-3}$ ) when using the TSI 3752, TSI 3790 and Brechtel 1720, respectively. Values in brackets indicate the maximal difference between the average and any point in the measurement. The effective density measurement exhibits some notable features, particularly at larger particle sizes. For all CPCs, there is a point at which the density starts to decrease, which occurs for sizes larger than  $\sim 1.5 \mu\text{m}$  for both the 3752 and 3790, and at approximately  $\sim 0.75 \mu\text{m}$  for the Brechtel 1720. These roll-offs are likely due to inertial losses within each CPC, which reduce the counting efficiency [168, 201] and increase the measured average charge. Note that the y-axis of Figure 7.4a has been truncated, and the effective density of the Brechtel 1720 CPC keeps decreasing as a function of size, explaining the spread in the reported measurement. If the analysis is restricted to particles less than  $1 \mu\text{m}$  in size, the agreement of the average density with the bulk density improves to within 8.3% for all CPCs. This work utilised a single counting efficiency factor to account for differences between the CPC and MSE. However, a size-dependent counting efficiency should be implemented, particularly above  $1 \mu\text{m}$ , where inertial losses can be significant, depending on the model of CPC. The density of ammonium sulphate was also measured, as it can form compact morphologies with particles that have a density close to the bulk value or agglomerates whose density decreases as a function of size [224, 229]. The average density of ammonium sulphate was found to be  $1686 \text{ kg m}^{-3}$  ( $\pm 144 \text{ kg m}^{-3}$ ),  $1709 \text{ kg m}^{-3}$  ( $\pm 124 \text{ kg m}^{-3}$ ), and  $1632 \text{ kg m}^{-3}$  ( $\pm 119 \text{ kg m}^{-3}$ ), for the TSI 3752, TSI 3790 and Brechtel 1720, respectively. Suggesting the production of compact particles.

There is a noticeable skew for both DOS and ammonium sulphate measurements, particularly for the TSI 3752 and Brechtel 1720 CPCs, which show an increase in density with particle size. This is particularly unexpected for DOS, which produces a spherical aerosol with a known bulk density. Some of these errors can potentially be explained by investigating how theoretical errors in measured quantities affect calculations of effective density. Figures 7.4c, d, and e show, theoretically, how errors in average charge, electrical mobility, and the CPMA mass-to-charge set-point affect average particle effective density measurements, respectively. Errors in the average charge or electrical mobility produce errors in effective density that are non-uniform across particle sizes due to the non-linearity of the Cunningham Slip correction with particle mobility size. In the free molecular regime, errors in effective density scale with  $1/\sqrt{\bar{q}}$  and  $\bar{Z}_p^{3/2}$ , whereas in the continuum regime, they scale with  $1/\bar{q}^2$  and  $\bar{Z}_p^3$  for charge and electrical mobility, respectively. These two limits are bridged within the transition regime, leading to non-linear error profiles in which errors are magnified at larger particle sizes. Errors in the CPMA mass-to-charge ratio correspond to equal errors in effective density that are not size-dependent, owing to the linearity between particle effective density and mass. Measurements for both the TSI 3752 and Brechtel exhibit similar non-linear skews in measurements until the counting efficiency of the measurements starts to decrease due to inertial roll-off.

It should be noted that numerical simulations detailed in Chapter 5 show that a small increase in the measured effective density as a function of size is expected, which is attributed to the finite widths of the particle charge distribution and transfer functions of the CPMA and MSE, resulting in small skewing of average quantities. However, this was less than 5% from 30 nm to 3000 nm, which is smaller than the increase observed experimentally. A possible explanation for these errors could be errors in the charge calibration or potentially non-linearity in the counting efficiency of the CPC. For instance, recent work by Sakurai et al. [167] demonstrated that a TSI 3752 may start to exhibit non-linear counting behaviour above concentrations of as little as  $2 \times 10^3 \text{ cm}^{-3}$ , which was attributed to insufficient correction for coincidence counting by the built-in correction algorithms. The point at which non-linear efficiency begins is well below the quoted single counting mode of the device,  $1 \times 10^5 \text{ cm}^{-3}$ . This means that a single value counting efficiency correction may introduce errors. Errors could also exist if the distribution exiting the CPMA is skewed in any way, which may affect the ability of the MSE to accurately determine the average electrical mobility, as discussed in Chapter 5. Notably, there is less skew exhibited by the TSI 3790 CPC, potentially because its concentration limit is  $1 \times 10^4 \text{ cm}^{-3}$ , and it is typically used for engine exhaust regulation, which requires linearity across its entire concentration range [51].

It is worth noting that the measurement of electrical mobility can be considered a free parameter in calibration, as it is only used to determine the average mobility diameter, which in turn is used to determine the average particle effective density. Therefore, electrical mobility measurement of the MSE could be calibrated by using a particle of a known effective density, in a similar manner to the work of Perraud et al. [155], who calibrated a CPMA-SMPS system using Santovac Oil, which has a known density. This could be beneficial for obtaining more accurate measurements of density and should be investigated in the future.

### 7.4.3 Distribution Validation: DOS and Ammonium Sulphate

Mobility distribution measurements of DOS and ammonium sulphate aerosols are depicted in Figure 7.5. The average effective density of the ammonium sulphate and DOS aerosol measured by the M<sup>2</sup>AS, as shown in Figure 7.5a, were 1742 kg m<sup>-3</sup> and 989 kg m<sup>-3</sup>, respectively, which are within 9% of the bulk density of each material, similar to the results discussed in the previous section. It is important to note that the validation of the effective density, as discussed in Section 7.4.2, was conducted independently from the measurements presented in this section. The errors in the effective density measurements are comparable in both Figure 7.4 and Figure 7.5, although the effective density axis ranges differ between the two figures. The measurements in this section are additionally fit to Equation 7.02 to obtain values for  $\rho_{100}$  and  $D_m$ , which are shown in Table 7.2. The values for  $\rho_{100}$  are within 4.5% of the bulk density of each material. Furthermore, the density exponents,  $D_m$ , are approximately equal (within 3.7%) to 3, indicating that the particles are close to spherical. However, all density exponents are slightly higher than 3, due to skew in the density measurement, as discussed in the previous section.

Figures 7.5b, c and d show the mobility distributions measured by the M<sup>2</sup>AS compared to an SMPS measurement of the same aerosol source. The mobility diameter distributions from the M<sup>2</sup>AS were found by converting the inverted mass distribution into mobility space using the measured effective density. Two different M<sup>2</sup>AS distributions are shown in each Figure: 'UDAC LC', which denotes corrections for only losses within the UDAC (per Figure 7.3), and 'UDAC + TF LC' function corrected distributions, which include both loss corrections for the UDAC and CPMA transfer function. The agreement between the M<sup>2</sup>AS distributions corrected for only UDAC losses and SMPS/CPC measurements ranged from 2.2% to 8.7% for the count median diameter ( $d_g$ ), 0.5% to 9.9% for the geometric standard deviation ( $\sigma_g$ ) and -24% to 10.7% for the number concentration ( $N$ ) measured by the combination of a CPC and Disc Diluter. The good agreement between  $d_g$  and  $\sigma_g$  validates the methodology to invert M<sup>2</sup>AS data. The agreements for the same parameters, when including the CPMA transfer losses, range from 2.6% to 29%, 11.1% to 17% and 35% to 93% for  $d_g$ ,  $\sigma_g$  and  $N$ ,

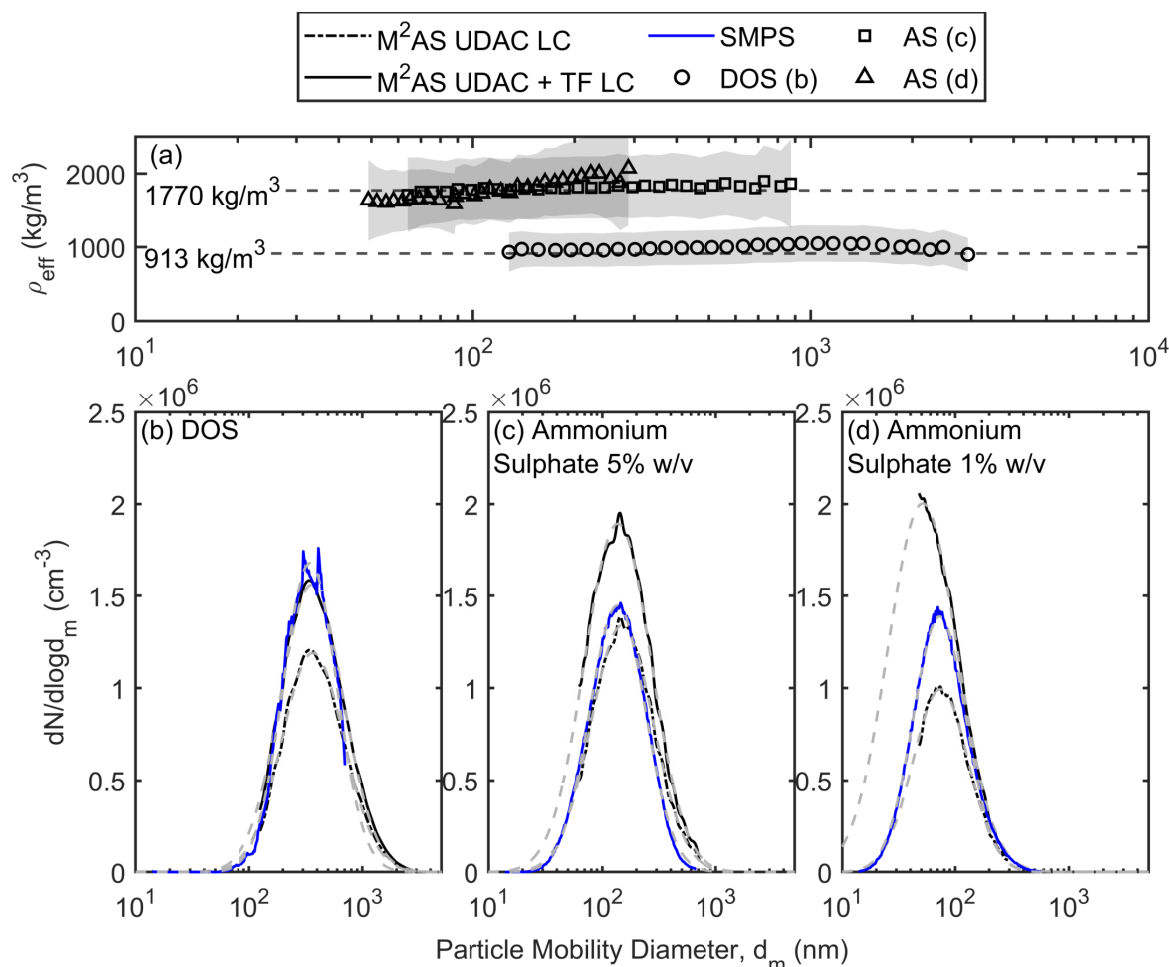


Fig. 7.5 Effective Density and mobility diameter distribution validation. Figure (a) shows effective density measured by the M<sup>2</sup>AS for DOS and ammonium sulphate. Figures (b), (c), and (d) show mobility distribution measurements from an SMPS (blue) compared to the M<sup>2</sup>AS corrected for UDAC losses denoted (M<sup>2</sup>AS UDAC LC, dashed black line), and the M<sup>2</sup>AS corrected for both UDAC losses and CPMA transfer function losses denoted (M<sup>2</sup>AS UDAC + TF LC, black line). Lognormal fits to data are shown in grey dashed lines.

respectively. It is clear that the loss correction function seems to be an overestimation of the losses within the system, and notably, the loss correction performs worse as particle size decreases. This is particularly evident in Figure 7.5d, where the distribution blows up fairly significantly - this results in both an overestimation in the total number concentration by close to a factor of 2, as well as a shifting of the distribution to smaller sizes.

These results suggest that the transmission through the CPMA used in this work is closer to theory than measured by Naseri et al. [133]. A new model of CPMA, the Mk2, was used in this study, which has a different inlet and outlet configuration to the Mk1, with the classification section remaining the same. This may be the cause of the discrepancy.

However, the inlet and exit paths in the Mk2 classifier are more convoluted than the original, which would likely act to reduce transmission efficiency, not increase them. There may also be discrepancies in the efficiency of transmission because the particles in the M<sup>2</sup>AS are highly charged. However, electrostatic losses due to charged particle dispersion would typically act to reduce transmission efficiency, not increase it [4]. Further work is required to understand losses within the CPMA better; this could be done through computational fluid dynamic models, which may enable more physically realistic loss functions to be determined than those currently available.

The integrated number concentration measured by the SMPS is in good agreement with CPC measurements ( $\leq 5.2\%$ ) for both ammonium sulphate measurements but exhibits poorer agreement (32%) for DOS measurements. The multiple charge correction for larger particle sizes is a known problem in SMPS measurements [219]. Despite using an impactor to remove larger particles, multiple charge artefacts can still be seen in the distribution, which exhibits sharp peaks near the mode of the distribution (Figure 7.5b).

It should be noted that in all measurements, the M<sup>2</sup>AS distribution is truncated, particularly at smaller particle sizes. A criterion that the total current measured by the MSE must be greater than 20 fA is imposed to ensure good quality data from the MSE. As discussed in the previous chapter, the M<sup>2</sup>AS measurement range is directly influenced by the amount of current available, resulting in a narrower measurement range compared to an SMPS, especially at smaller sizes. However, the M<sup>2</sup>AS can measure particles greater than 1  $\mu\text{m}$ , which is not possible with SMPS systems.

#### 7.4.4 Non-spherical Particle Validation

Comparison of effective density measurements from the M<sup>2</sup>AS and CPMA-SMPS of soot particles are shown in Figure 7.6. There is good agreement between the two measurement techniques; this is demonstrated through least squares fitting to obtain values of  $D_m$  and  $\rho_{100}$  which describe the average relationship between mass and mobility. For all soot sources, the density pre-factor is within 10% and the density exponent within 5% between the two methods, indicating that the M<sup>2</sup>AS can suitably measure the average effective density of non-spherical aerosols relative to the traditional analysis methods of the CPMA-SMPS. Although the global fits are in good agreement with one another, there is some skew in the experimental data, such as that seen at the end of the effective density measurement in Figure 7.6 (a), in which the density seemingly starts to increase at the larger particle sizes or the slight s-shaped curves exhibited in the Figures 7.6b and c, d. Furthermore, although it is hard to directly compare measurements between the two methods as the size selection method is slightly different, individual measurement points exhibit up to  $\sim 20\%$  differences. However, these

Table 7.2 Comparison of M<sup>2</sup>AS measurements to SMPS and CPC measurements of DOS and ammonium sulphate (AS). Distribution and density parameters were determined through least squares minimisation to the experimental data. Numbers in brackets indicate one standard deviation of a minimum of three repeats of each measurement. UDAC LC denotes data corrected for only UDAC losses, UDAC + TF LC denotes data corrected for both UDAC losses and losses within the CPMA.

| Aerosol   | Instrument                     | $N$ ( $10^5 \text{ cm}^{-3}$ ) | $d_g$ (nm)     | $\sigma_g$   | $\rho_{100}$ ( $\text{kg m}^{-3}$ ) | $D_m$       |
|-----------|--------------------------------|--------------------------------|----------------|--------------|-------------------------------------|-------------|
| DOS       | CPC                            | 7.47 (0.05)                    | -              | -            | -                                   | -           |
|           | SMPS                           | 9.83 (0.11)                    | 347 (1.4)      | 1.71 (0.01)  | -                                   | -           |
|           | M <sup>2</sup> AS UDAC LC      | 8.27 (0.09)                    | 364 (1.93)     | 1.88 (0.001) | 950 (15.9)                          | 3.04 (0.01) |
|           | M <sup>2</sup> AS UDAC + TF LC | 11.0 (0.11)                    | 356 (1.68)     | 1.90 (0.01)  |                                     |             |
| AS 5%w/v  | CPC                            | 9.48 (0.27)                    | -              | -            | -                                   | -           |
|           | SMPS                           | 9.09 (0.31)                    | 136 (2.1)      | 1.77 (0.01)  | -                                   | -           |
|           | M <sup>2</sup> AS UDAC LC      | 9.04 (0.19)                    | 149 (1.68)     | 1.89 (0.01)  | 1845 (39.9)                         | 3.01 (0.01) |
|           | M <sup>2</sup> AS UDAC + TF LC | 13.6 (0.25)                    | 136 (1.87)     | 1.97 (0.02)  |                                     |             |
| AS 1% w/v | CPC                            | 7.82 (0.27)                    | -              | -            | -                                   | -           |
|           | SMPS                           | 8.23 (0.23)                    | 71.00 (1.75)   | 1.70 (0.02)  | -                                   | -           |
|           | M <sup>2</sup> AS UDAC LC      | 5.94 (0.11)                    | 72.58 (1.43)   | 1.75 (0.01)  | 1763 (28.9)                         | 3.10 (0.02) |
|           | M <sup>2</sup> AS UDAC + TF LC | 15.0 (1.02)                    | 51.08 (1.0298) | 1.98 (0.04)  |                                     |             |

differences lie within the combined measurement uncertainties. Ultimately, the differences between the two measurement techniques are not dissimilar to similar comparisons of other tandem classification systems [89, 224].

Figure 7.7 presents a comparison of the mobility distributions measured with the SMPS and the M<sup>2</sup>AS for different soot aerosols. The lognormal fits to the data are shown in Table 7.3. For the UDAC loss-corrected M<sup>2</sup>AS distributions, the  $d_g$  of the M<sup>2</sup>AS distributions is consistently higher than that of the SMPS, with differences ranging from 5.5% to 26%. The GSD is systematically narrower by -9.1% to -5.1%. The consistently larger  $d_g$  could be attributed to uncertainties in the experimentally determined effective density relation, which, as discussed in Chapter 6, introduce greater uncertainty in the determined mass distribution. Another likely explanation is related to the conversion between mass and mobility space. The M<sup>2</sup>AS measurement of effective density reflects the average of the CPMA-classified aerosol population. As discussed in Chapter 5, the measured effective density will exhibit errors relative to the geometric mean effective density relation of the underlying aerosol. Therefore, as demonstrated in Section 6.5.4 of Chapter 6, this results in errors when converting from the inverted mass distribution to a different property. For measurements where a total concentration was taken (Cast setting 3 and DPG Soot), the M<sup>2</sup>AS with only UDAC loss

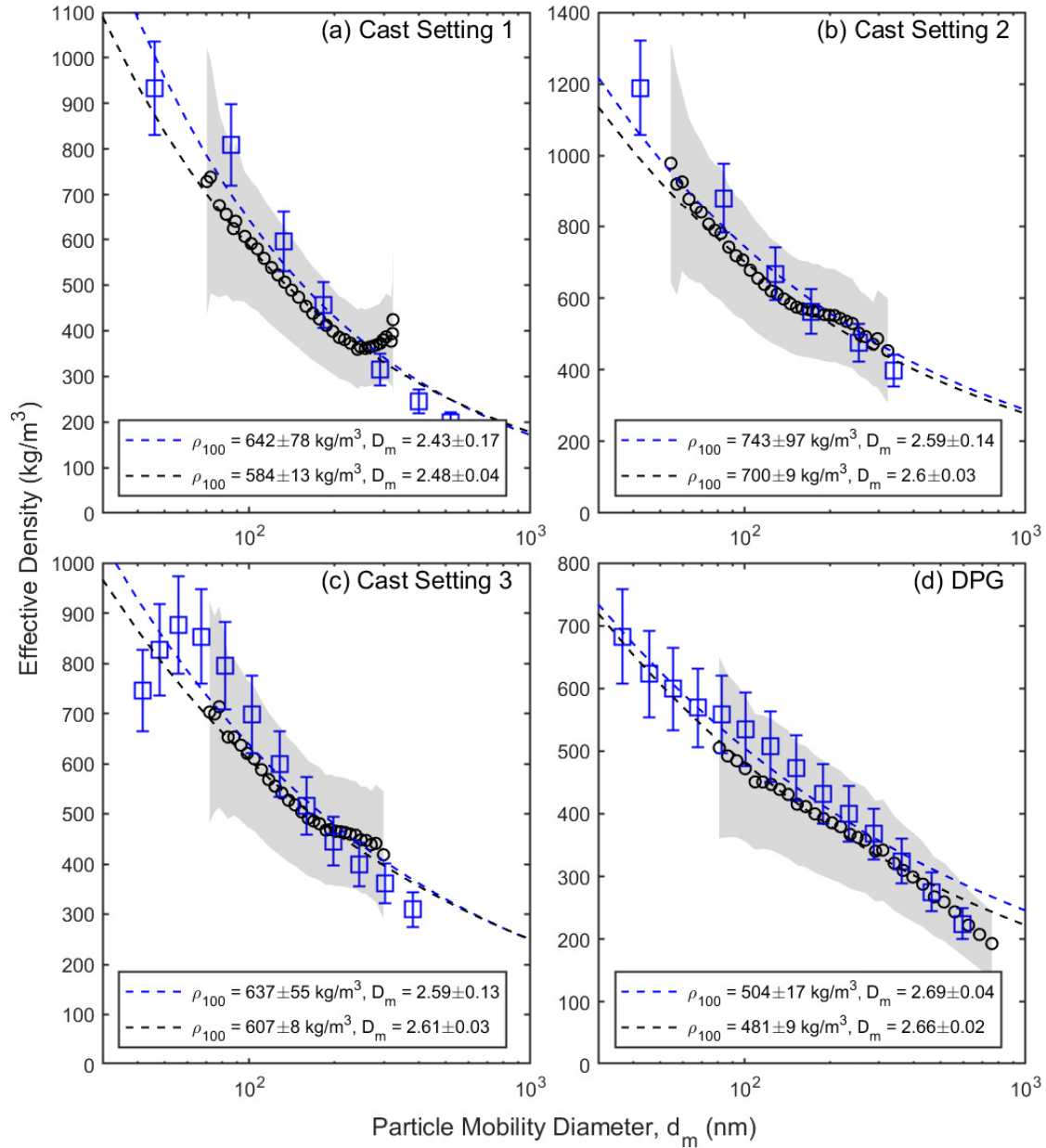


Fig. 7.6 Comparison of effective density measurements between a CPMA-SMPS (blue squares) and M<sup>2</sup>AS (black circles). Dashed lines of the same colours indicate fits to the corresponding data, which yield values  $D_m$  and  $\rho_{100}$ , shown in the legend. Uncertainties in the legend indicate 95% confidence interval in the fit. Error bars in CPMA-SMPS measurements only include Type B uncertainties, equal to 9.4%. The grey shaded area indicates uncertainties in M<sup>2</sup>AS measurements, including Type A and Type B uncertainties.

correction underestimates the total concentration by between 16.8 - 30.5%. Compared to the total concentration obtained from SMPS measurements, the M<sup>2</sup>AS with only UDAC losses

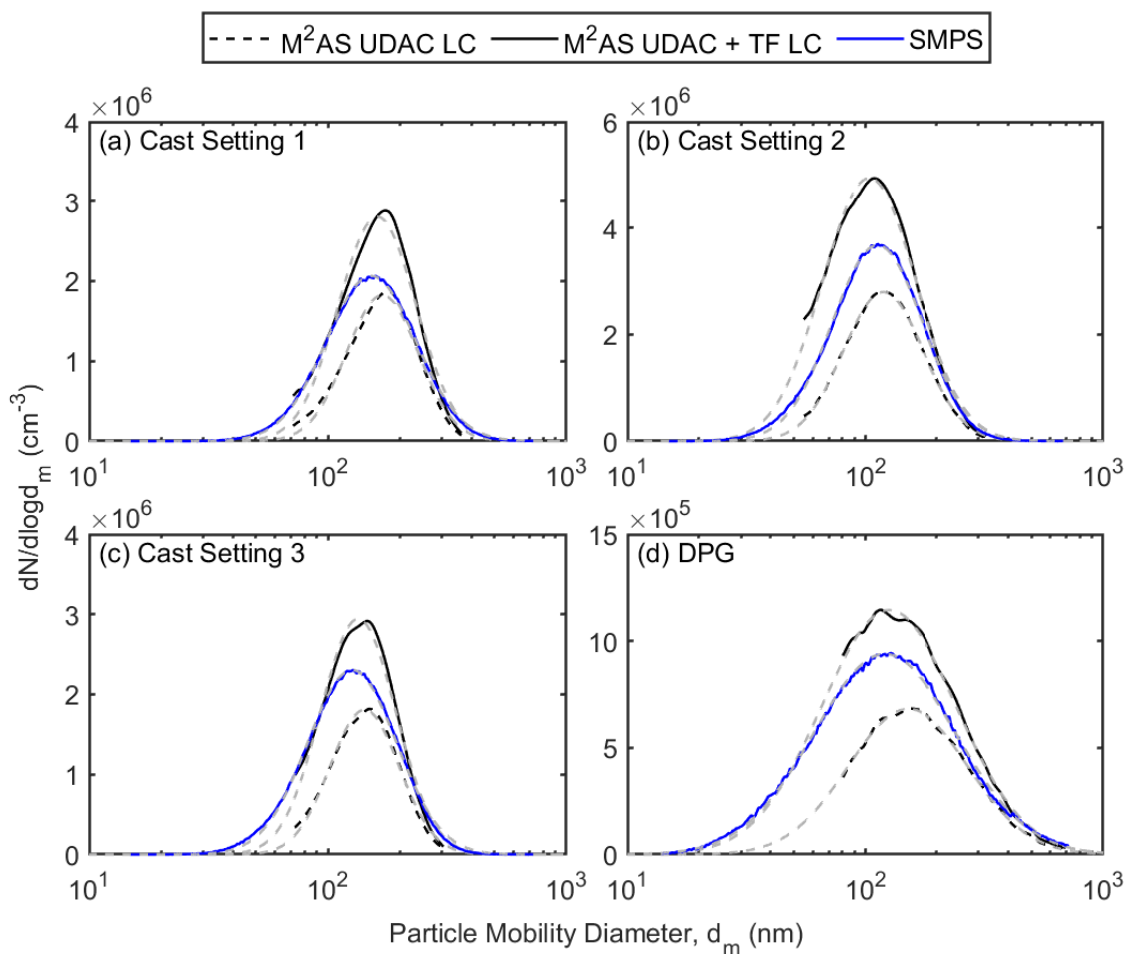


Fig. 7.7 SMPS mobility distributions (blue) compared to the M<sup>2</sup>AS measurements corrected for UDAC losses denoted (M<sup>2</sup>AS UDAC LC, dashed black line), and the M<sup>2</sup>AS corrected for both UDAC losses and CPMA transfer function losses denoted (M<sup>2</sup>AS UDAC + TF LC, black line). Lognormal fits to data are shown in grey dashed lines.

included under-estimates the particle concentration by 34% - 48%. However, it should be noted that the SMPS seemingly overestimates total concentration relative to the CPC by up to 26%. Soot aerosols charge more readily than spherical particles, resulting in a different steady-state charge distribution. This can potentially result in distortions in particle size distribution measurements of the SMPS [81, 221, 123].

In all cases, the inclusion of the CPMA loss function shifts the distribution to the left in mobility space and increases its width, improving agreement with the SMPS. This adjustment brings the deviation in  $d_g$  to between -7.3% and 5.5%, while the geometric standard deviation is within -5.2% to 1%. However, after correcting for transfer function losses, the number

concentration is overestimated relative to the SMPS by 12% - 35% and the CPC by 34% - 49.6%.

Table 7.3 Comparison of M<sup>2</sup>AS measurements to SMPS and CPC measurements. Size distribution and density parameters were determined by fit to experimental measurements. Numbers in brackets indicate one standard deviation of a minimum of two repeats of each measurement.

| Aerosol        | Instrument                     | $N$ ( $10^5 \text{ cm}^{-3}$ ) | $d_g$ (nm)    | $\sigma_g$    |
|----------------|--------------------------------|--------------------------------|---------------|---------------|
| Cast Setting 1 | CPC                            | -                              | -             | -             |
|                | SMPS                           | 10.04 (0.47)                   | 152.6 (0.96)  | 1.54 (0.003)  |
|                | M <sup>2</sup> AS UDAC LC      | 6.75 (0.13)                    | 169.8 (0.53)  | 1.42 (0.004)  |
|                | M <sup>2</sup> AS UDAC + TF LC | 11.25 (0.02)                   | 161.5 (0.37)  | 1.46 (0.004)  |
| Cast Setting 2 | CPC                            | -                              | -             | -             |
|                | SMPS                           | 17.67 (0.14)                   | 112.8 (0.66)  | 1.55 (0.002)  |
|                | M <sup>2</sup> AS UDAC LC      | 11.62 (0.18)                   | 119.1 (0.1)   | 1.47 (0.0001) |
|                | M <sup>2</sup> AS UDAC + TF LC | 24.03 (0.34)                   | 103.8 (0.03)  | 1.57 (0.0005) |
| Cast Setting 3 | CPC                            | 8.34 (0.06)                    | -             | -             |
|                | SMPS                           | 10.52 (0.21)                   | 125.8 (0.54)  | 1.54 (0.003)  |
|                | M <sup>2</sup> AS UDAC LC      | 6.94 (0.27)                    | 140.5 (1.7)   | 1.40 (0.005)  |
|                | M <sup>2</sup> AS UDAC + TF LC | 12.48 (0.62)                   | 131.2 (2.11)  | 1.45 (0.01)   |
| DPG            | CPC                            | 6.31 (0.27)                    | -             | -             |
|                | SMPS                           | 7.02 (0.20)                    | 118.7 (1.59)  | 1.97 (0.015)  |
|                | M <sup>2</sup> AS UDAC LC      | 4.38 (0.067)                   | 149.9 (1.45)  | 1.79 (0.005)  |
|                | M <sup>2</sup> AS UDAC + TF LC | 8.47 (0.32)                    | 122.56 (3.31) | 1.95 (0.03)   |

#### 7.4.5 Preliminary comparisons of M<sup>2</sup>AS measurements with two-dimensional mass-mobility measurements

The CPMA-SMPS system can obtain two-dimensional mass-mobility data through inversion techniques [178, 161, 180]. Here, a two-dimensional mass-mobility distribution is obtained from the inversion of CPMA-SMPS data for the Cast setting 3 soot. The data was inverted using the methods and code described by Sipkens et al. [178]. Figure 7.8 shows the full mass-mobility distribution obtained through this inversion method, with marginal mobility and mass distributions shown as solid black lines at the top and to the right of the two-dimensional distribution. The marginal distributions for each particle metric are obtained

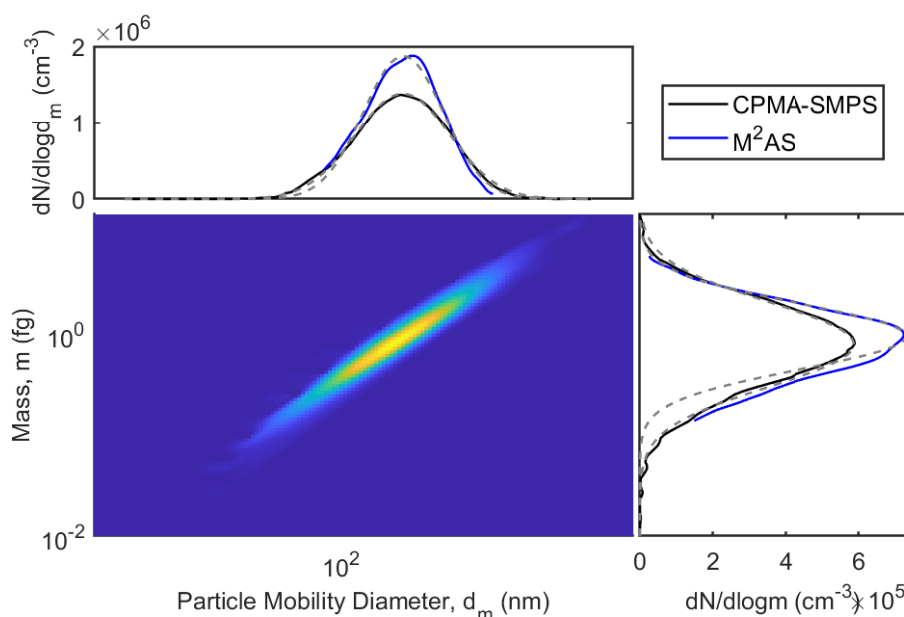


Fig. 7.8 Reconstructed mass-mobility distribution for Cast setting 3 soot, where the brightness of the contour plot corresponds to the number concentration of particles on a linear scale. Marginal distributions (solid black lines) for each of the variables are shown on the corresponding axis, found by integrating the distribution in the corresponding direction. Also shown is the measured marginal distribution obtained from M<sup>2</sup>AS measurements (solid blue lines). Dashed grey lines indicate lognormal fits with fit parameters shown in Table 7.4.

by integrating the two-dimensional distribution. Also shown in blue is the corresponding distribution obtained from M<sup>2</sup>AS measurements.

The total aerosol concentration is ignored in this analysis, which scales the integrated area of each distribution, and instead focuses on comparing the width and mean of the distributions, as shown in Table 7.4. This decision was made because the CPMA was operated at  $0.3 \text{ L min}^{-1}$  with higher resolution for CPMA-SMPS measurements and at  $1 \text{ L min}^{-1}$  for M<sup>2</sup>AS measurements. These differences may affect the losses within the CPMA, and based on the results from previous sections, the proposed CPMA loss correction is the greatest source of uncertainty for M<sup>2</sup>AS measurements. Therefore, the M<sup>2</sup>AS data shown has only been corrected for losses within the UDAC.

The difference between the mode and geometric standard deviation of the mobility distribution is consistent with the comparison performed with the SMPS measurements, with the M<sup>2</sup>AS measuring a distribution that is shifted to the right in mobility space. As previously mentioned, this could be due to a skew in the average effective density measured by the M<sup>2</sup>AS relative to the underlying geometric mean relationship of the distribution. This reasoning is

illustrated in Figure 7.9, which shows the underlying effective density distribution compared with M<sup>2</sup>AS measurements. It is evident that the average effective density is skewed about the geometric mean density line, obtained from the full two-dimensional mass-mobility distribution. The accuracy of the M<sup>2</sup>AS data improves closer to the distribution's geometric mean diameter. Furthermore, the density exponent determined from M<sup>2</sup>AS measurements is larger (indicating a steeper gradient in mass-mobility space) than that determined from the full two-dimensional inversion (2.59 vs. 2.29), which is in qualitative agreement with the numerical model discussed in Chapter 5.

The geometric mean of the mass distribution, determined through fitting, is approximately 19.2% larger for M<sup>2</sup>AS measurements compared to the marginal distribution obtained from CPMA-SMPS measurements. The cause of this discrepancy is unclear. It could stem from unaccounted losses in the CPMA, which may act to alter distributions slightly. Moreover, the losses likely differ between CPMA-SMPS measurements relative to M<sup>2</sup>AS measurements due to the different flow rates and rotational speed profiles used in each measurement. Additionally, the uncertainty in mass space is likely more significant for tandem classification measurements, as CPMA-SMPS data is sparser in mass than in mobility space. Since parameters from the two-dimensional distribution were derived by fitting bivariate lognormal distributions to the mass-mobility reconstructions, there may be larger uncertainties in these parameters due to the increased complexity of tandem instrumentation and their associated transfer functions [179, 183]. Further work is required to better understand and compare M<sup>2</sup>AS measurements with those obtained through tandem measurement systems.

Table 7.4 Comparison of M<sup>2</sup>AS measurements to those obtained through two-dimensional distribution inversion for Cast Setting 3 soot.

| Aerosol        | Instrument        | $d_g$ (nm) | $\sigma_g$ | $m_g$ (fg) | $\sigma_m$ | $\sigma_{m d}$ | $\rho_{100}$ (kg m <sup>-3</sup> ) | $D_m$ |
|----------------|-------------------|------------|------------|------------|------------|----------------|------------------------------------|-------|
| CAST Setting 3 | CPMA-SMPS         | 140        | 1.50       | 0.78       | 2.59       | 1.25           | 694                                | 2.29  |
|                | M <sup>2</sup> AS | 141        | 1.41       | 0.93       | 2.1        | -              | 637                                | 2.59  |

#### 7.4.6 Comparison of Particle Charge Measurements

The comparison between the charging of different aerosol morphologies has been of interest to many authors. The measurements of particle charge for all size distribution measurements are shown in Figure 7.10. There is a clear trend that non-spherical particles acquire more charge than DOS and ammonium sulphate for the same mobility size. More specifically, it was found that non-spherical particles, on average, charge between 10–25% more than spherical/compact particles. This agrees well with previous literature on particle charging

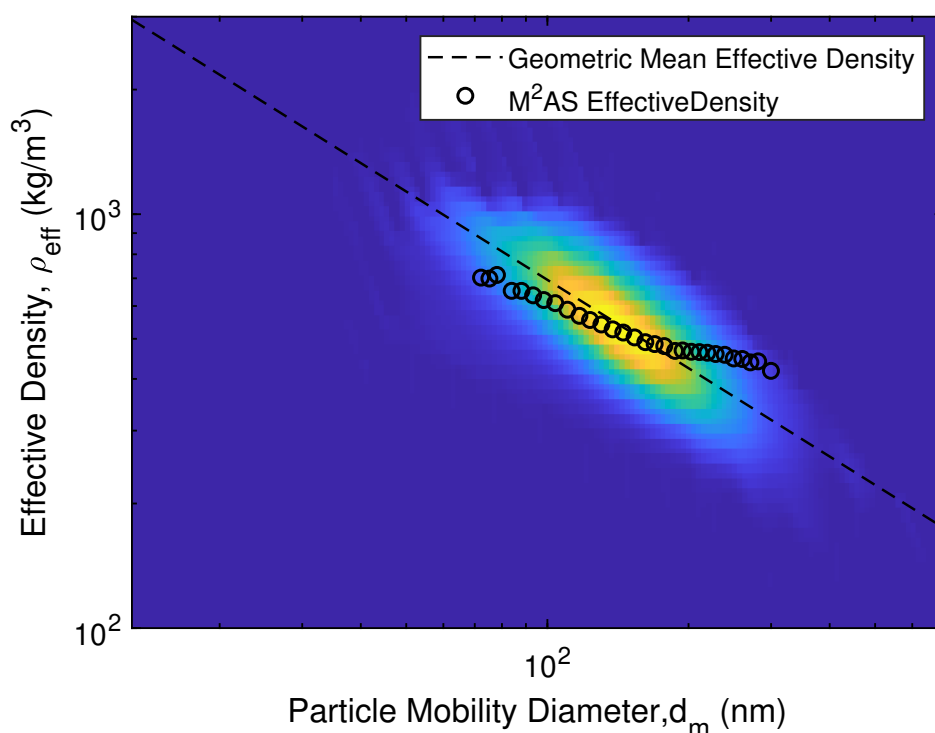


Fig. 7.9 Two-dimensional representation of the effective density-mobility distribution. Also shown is the geometric mean effective density relation (black dashed line) and M<sup>2</sup>AS measurements of the average particle effective density.

involving comparisons between compact particles and soot aerosols [85, 144, 175] as well as the results from Chapter 4. The M<sup>2</sup>AS provides an opportunity to enhance understanding of the relationship between mobility size, particle morphology, and particle charge across a wide size range and obtain better relationships for charge equivalent diameters which can be utilised in inversion schemes in other instrumentation which utilise unipolar chargers [150, 230].

#### 7.4.7 Mass and Aerodynamic Distributions

The resulting discussion focused on the comparison of mobility distributions. However, the intended purpose of the M<sup>2</sup>AS is to measure particle mass distributions. Therefore, the mass distributions of all measurements have been collated, shown in Figure 7.11a. The M<sup>2</sup>AS can measure over 5 orders of magnitude of mass, 0.07 fg to 10000 fg of aerosols. Furthermore, the mass distributions can be converted to mass-weighted distributions by multiplying the mass number weighted distribution by the particle mass, as shown in Figure 7.11b. These

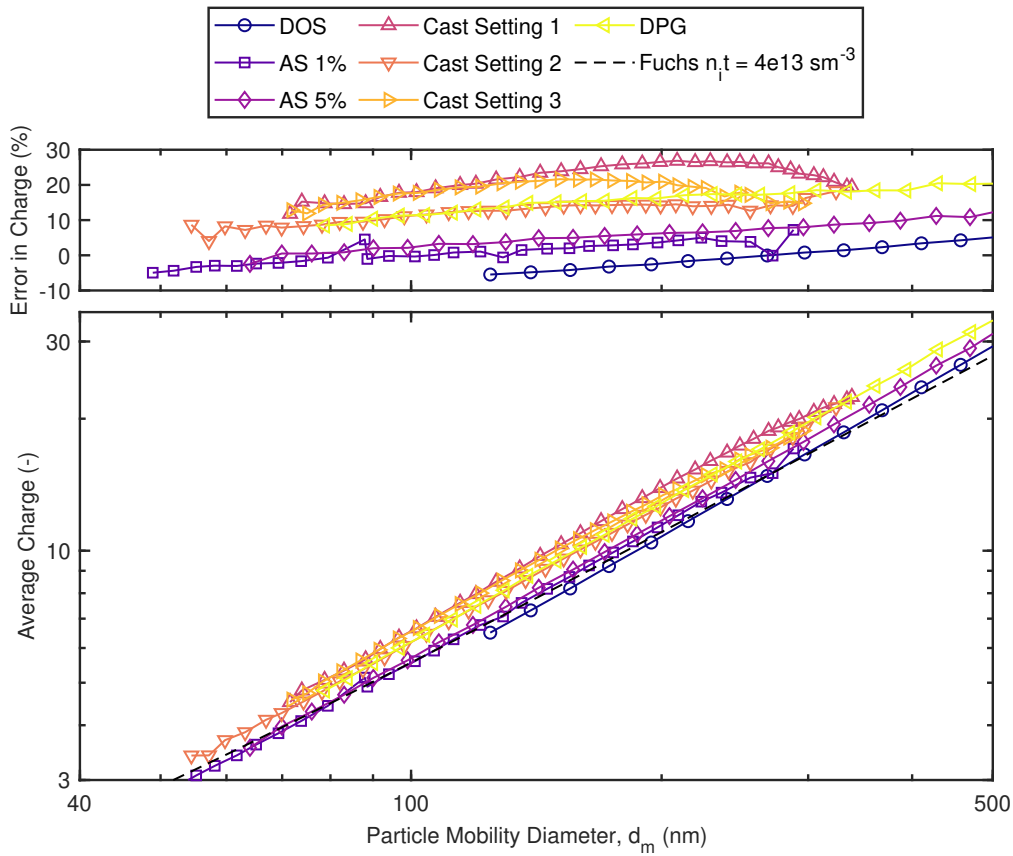


Fig. 7.10 Particle average charge as a function of mobility diameter for all the distribution measurements taken in the preceding sections. The top figure illustrates percentage differences between the measured average charge and Fuchs' model [49] evaluated at an  $n_{it} = 4 \times 10^{13} \text{ s m}^{-3}$ . The bottom Figure illustrates the measured average charge as a function of mobility diameter for all the distribution measurements taken in the preceding sections. For greater clarity, the charge comparison is limited to between 50 nm and 500 nm, which represents the intersection of the distributions measured in this work. Error bars are not included for clarity. However, bias uncertainties in mobility diameter and charge are approximately 7% and 5%, respectively.

mass distributions better highlight that the measurements of the  $M^2AS$  are limited at the smallest and largest sizes due to smaller current signals. Note that the mass distributions in Figure 7.11b can be integrated to determine the total mass concentration; however, this is likely to be in error for two reasons. Firstly, uncertainty in the losses within the CPMA transfer function will propagate into integrated quantities, as previously discussed, for the total number concentration. Secondly, the transfer function of the CPMA has only been validated up to 500 nm. The use of a unipolar charger increases the sizing limit of the CPMA past 3000 nm, and therefore, inertial loss is likely to be an important consideration of particle

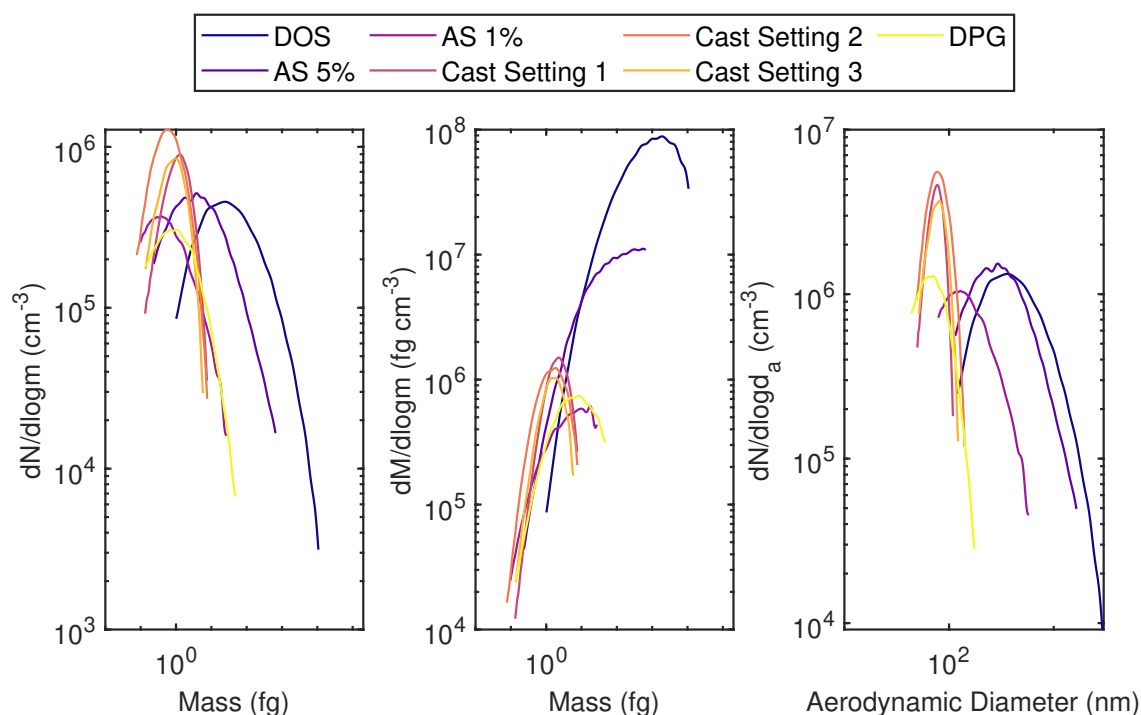


Fig. 7.11 Size distributions of the aerosols measured in this work shown in other property spaces. Figure (a) shows the number-weighted mass distribution,  $dN/d\log m$ , (b) the mass-weighted mass distribution  $dM/d\log m$  and (c) the number-weighted aerodynamic size distribution,  $dN/d\log d_a$ .

losses within the CPMA. Finally, Figure 7.11c shows the aerodynamic size distributions. The ability to obtain any equivalent distribution from a single measurement system distribution is particularly useful. However, as discussed in Chapter 6, the aerodynamic distributions of soot and other morphologically diverse aerosols are likely to be in error due to the broad range of morphologies present in a given population. However, this could be confirmed in future work through comparison with aerodynamic measurements such as those obtained with the AAC.

## 7.5 Conclusions

This work presents the experimental validation of the Mass Mobility Aerosol Spectrometer (M<sup>2</sup>AS), demonstrating its capability to measure particle mass, mobility, and effective density across a wide range of aerosols. The M<sup>2</sup>AS was able to measure the average effective density of DOS and ammonium sulphate within 15% of the bulk density from 30 nm to 3000 nm, with improved agreement to within 8.2% for particles smaller than 1  $\mu$ m. However, some skew

in density measurements was observed, likely due to errors in average charge or electrical mobility. Caution is recommended for particles larger than 1  $\mu\text{m}$ , as inertial losses in the CPC impact counting efficiencies and charge measurements.

In terms of mobility distributions, the  $M^2AS$  showed good agreement with SMPS measurements for the geometric mean diameter and standard deviation, with discrepancies within 10%. However, larger differences were observed in total concentration, particularly when correcting for CPMA losses, with up to a two-fold overestimation at smaller particle sizes.

For non-spherical soot particles, the mass-mobility relationship constants derived from  $M^2AS$  measurements were within 10% of those obtained from CPMA-SMPS, though individual data points showed deviations of up to 20%. The  $M^2AS$  also systematically measured larger mobility distributions than the corresponding SMPS results. This is likely due to the limitations of applying a single-valued mass-mobility relation to particles with varying morphologies. A preliminary comparison with the two-dimensional inversion of CPMA-SMPS measurements confirmed this effect, indicating that the effective density measured by the  $M^2AS$  deviates from the geometric mean relationship. These differences in distribution and morphological parameters highlight areas for further investigation.

Overall, the  $M^2AS$  demonstrates reliable performance in measuring particle mass, mobility, and effective density across a variety of aerosol types. Operating at a flow rate of  $1\text{ L min}^{-1}$ , the instrument covers a mobility size range of 30 nm to 3000 nm and an equivalent mass range from 0.05 fg to 30000 fg. The uncertainties associated with effective density measurements are approximately 20%. Given that the MSE constitutes a key component of the  $M^2AS$ , the limiting single-charge particle number concentration downstream of the CPMA is  $1.5 \times 10^4\text{ cm}^{-3}$ , as detailed in Chapter 5. Due to its wide measurement range and relatively short measurement time (15–20 minutes), the  $M^2AS$  could be applied across a variety of contexts, including the assessment of combustion agglomerates, engineering powders, spray-dried materials, coated particles, and carbon nanotubes. However, its application to externally mixed aerosols remains to be explored, as the concept of an average effective density can become ambiguous when two aerosol populations with significantly different densities are measured at the same particle mass.

Nonetheless, opportunities remain to enhance the system, particularly through improved density measurements and a deeper understanding of the CPMA transfer function, which will serve to increase the accuracy of integrated metrics such as total number concentration.



# Chapter 8

## Conclusions and Future Work

### 8.1 Thesis Conclusions

This thesis aimed to advance the understanding of particle charging and classification, with two main objectives: investigating the influence of humidity on particle charging mechanisms and enhancing the application of unipolar charger–CPMA systems.

This work has resulted in several key accomplishments:

- A comprehensive experimental investigation of the effects of relative humidity on a range of aerosol charging mechanisms (bipolar, unipolar, and photoelectric).
- In-depth numerical and experimental evaluation of the limitations and challenges of multiple charge correction and charge–mobility relationships in aerosol instrumentation.
- Experimental validation of the Interpolated Average Charge (INTAC) algorithm for unipolar charger–CPMA systems.
- The theoretical and experimental validation of a novel classifier: the Mobility Separator Electrometer (MSE).
- The numerical and experimental validation of a novel measurement system: the Mass–Mobility Aerosol Spectrometer ( $M^2AS$ ), capable of directly measuring mass, mobility, and charge in real time.

The first objective, described in Section 2.4, was addressed by examining how humidity affects various charging mechanisms, particularly in the context of their impact on average charge measurements, which is crucial for low-cost sensing applications. Measurements on

size-selected aerosols revealed that humidity influences each charging mechanism differently. For radioactive bipolar chargers, an increase in relative humidity led to a more positive mean charge, indicating an increase in the ion mobility ratio. In contrast, unipolar diffusion charging within a current-controlled corona charger was relatively unaffected by humidity variations. For direct UV photoelectric chargers, increasing humidity resulted in a decrease in the charge per particle attributed to UV light attenuation within the charging chamber.

Measurements of ions produced from unipolar and bipolar diffusion chargers using a High-Resolution DMA further demonstrated that humidity significantly alters the ion distribution. A comparison between ion measurements and mean charge measurements for the bipolar charger showed a consistent trend towards more positive particle charges; however, the magnitude of this trend differed between ion and particle charge measurements.

The remainder of this thesis focused on validating and improving methods for unipolar charger–CPMA systems. The Interpolated Average Charge Algorithm (INTAC) was experimentally validated as an effective multiple charge correction method for these systems. INTAC uses power law functions to relate average charge and mass to mobility diameter. The primary source of uncertainty in the INTAC algorithm stems from the mass–mobility relationship. Additionally, aggregates receive more charge than spheres of the same mobility size, leading to an underestimation of the average charge compared to the actual transmitted charge. Despite these challenges, the INTAC algorithm can estimate the average transmitted mass within  $\pm 20\%$  accuracy if power law values are experimentally determined. This study highlighted the main challenge of multiple charge correction in unipolar charger–CPMA systems: the uncertainty in the relationship between mass, mobility, and charge.

To address the limitations of multiple charge correction, a new classifier, the Mobility Separator Electrometer (MSE), was introduced and validated. The MSE measures particle electrical mobility using closed-loop voltage control. Its theoretically derived transfer function showed good agreement with experimental results. The MSE's strength lies in tandem applications, where it is combined with existing instrumentation, such as a unipolar diffusion charger, upstream classifier, and CPC. Numerical simulations demonstrated that this tandem system enables real-time multiple charge correction, providing accurate particle mobility diameter measurements. However, it was observed that 'average' measurements from these systems can be skewed for aerosol distributions containing non-spherical particles, such as soot, due to interactions between classifier transfer functions and the aerosol's morphological characteristics. Nevertheless, a tandem system comprising a unipolar diffusion charger, AAC, MSE, and CPC successfully measured the average density of compact aerosol particles to within 8.5% of the bulk material density.

Building on the MSE validation, numerical simulations were conducted to explore the challenges of determining particle mass distributions using unipolar charger–CPMA systems. The inherent uncertainties in the relationships between particle mass, mobility, and charge make these systems susceptible to errors when employing inversion techniques. To overcome these issues, a new measurement system, the Mass–Mobility Aerosol Spectrometer ( $M^2AS$ ), was developed. The  $M^2AS$  utilises the MSE within a tandem configuration (UDAC–CPMA–MSE–CPC) to enable direct measurement of mass, mobility, and charge, thus eliminating sensitivity to perturbations in any of these quantities. However, the  $M^2AS$  has two main limitations. First, converting its measurements to other particle property domains using the effective density relation can be erroneous when dealing with morphologically diverse aerosols. Second, the system’s accuracy depends on sufficient aerosol concentration, as the MSE requires adequate current to measure charge and mobility effectively.

The final chapter of this thesis provides experimental validation of the  $M^2AS$  system, demonstrating its capability as a tool for measuring aerosol properties, including particle mass, mobility, and effective density. The results showed that the  $M^2AS$  provides accurate measurements within a reasonable margin of error (10%) for particles smaller than 1  $\mu m$  for effective density. Validation against traditional methods such as SMPS and CPMA–SMPS highlighted areas of strong agreement (within 10%), such as geometric mean diameter and standard deviation of DOS and ammonium sulphate distributions, as well as the mass–mobility parameters for soot aerosols. However, some discrepancies were noted, particularly in the measurement of total concentration and the handling of non-spherical particles, which were systematically sized larger in mobility space by the  $M^2AS$  relative to the SMPS. Preliminary comparisons to reconstructed two-dimensional mass–mobility distributions corroborated numerical models within previous chapters, concluding that the  $M^2AS$  measures an effective density skewed relative to the underlying geometric mean relationship.

## 8.2 Impacts of Research

This research contributes significantly to the field of aerosol measurement by addressing key challenges related to particle charging and classification. The experimental insights into humidity effects on charging mechanisms provide important guidance for improving the accuracy and reliability of charging-based aerosol instruments. This is particularly relevant for researchers and instrument developers working in ambient, industrial, and combustion aerosol monitoring, where environmental conditions can vary widely and affect sensor performance. Furthermore, these findings may impact SMPS measurements in ambient

environments, where it is generally assumed that particles attain a steady-state charge distribution—an assumption that may not hold under varying humidity conditions.

Validation of the INTAC algorithm enables practitioners using CERMS for mass concentration calibration or measurement of mass-absorption cross-sections to confidently determine the average transmitted mass, provided the mass-mobility relationship and charging performance of the aerosol being measured are well characterised.

Moreover, the development and validation of novel instruments, such as the Mobility Separator Electrometer (MSE) and the Mass–Mobility Aerosol Spectrometer ( $M^2AS$ ), offer practical advances for real-time measurement of particle mass, mobility, and effective density without relying on simplifying assumptions. These tools facilitate a more complete aerosol characterisation in applications ranging from process engineering to combustion analysis. By improving multiple charging corrections and enabling direct mass measurements, this work supports the design of more robust and accurate aerosol measurement systems, benefiting both scientific research and applied sectors such as materials processing.

## 8.3 Future Work

### 8.3.1 On the effect of humidity on particle charging

Whilst the work on humidity provided valuable insights into the effects of water vapour concentration on charging mechanisms, several questions remain unanswered, and further refinement of both the findings and the techniques used to investigate them is necessary.

Firstly, the humidity control used in these experiments was constrained by the lack of a temperature-controlled laboratory environment, which limited the precision with which water vapour content could be adjusted. Enhanced humidity regulation would enable finer control over water vapour concentration, allowing for more detailed investigations into its impact on particle charging mechanisms. Furthermore, varying both temperature and humidity simultaneously would provide an opportunity to assess whether similar water vapour concentrations at different temperatures — and thus different relative humidities — have the same effect on particle charging. This would help clarify whether the effects of humidity are temperature-dependent, improving the understanding of how environmental conditions influence charging processes.

Additionally, a discrepancy was observed between ion measurements and mean charge measurements for the bipolar chargers used in this work. A deeper exploration of the literature revealed that similar discrepancies have been reported by other researchers. Addressing these discrepancies is crucial for refining experimental techniques, such as the HRDMA, and for

improving numerical models that rely on ion properties as inputs. One potential avenue for progress would involve pairing ion mobility measurements with mass spectrometry analysis. This would provide a more comprehensive understanding of how both the mobility and mass of ions are affected by humidity. Such an approach would offer valuable insights into the interactions between carrier gas vapour concentration and charging ions, which could ultimately lead to the development and validation of more accurate charging models.

### 8.3.2 On the Mass Mobility Aerosol Spectrometer

Despite the successes of this work, several aspects remain in improving the precision and extending the capabilities of the M<sup>2</sup>AS. The most notable of these include refining the measurement of effective density, understanding the CPMA transfer function more thoroughly, and improving the treatment of particles with complex morphologies. These improvements will enhance the M<sup>2</sup>AS's accuracy and broaden its applicability to a wider range of aerosol types.

The skew in effective density can be more readily investigated by measuring electrical mobility distribution and mobility distribution downstream of the CPMA in the M<sup>2</sup>AS. This can be performed using an SMPS system. If the bipolar charger is bypassed, the electrical mobility distribution of the CPMA-classified aerosol can be measured. The mobility distribution can then be measured by passing the classified aerosol through the bipolar charger. These distributions can be compared to parallel measurements of average values obtained by the combination of the MSE and CPC.

As with the development of any new measurement system, there are numerous scenarios that warrant further investigation and improvement. The charger in the M<sup>2</sup>AS could be enhanced, particularly to address the reduction in signal strength caused by dilution flows, which currently limits the measurement range of the system. The CPMA transfer function also requires further investigation, especially concerning the loss functions used in this work, which are currently non-physical. A more fundamental understanding of aerosol loss within the CPMA is essential, and this could benefit from the application of full computational fluid dynamics (CFD) models. Furthermore, it is important to note that the M<sup>2</sup>AS has been validated with only a single CPMA. To assess reproducibility more effectively, future measurements should involve different CPMAs to confirm the system's consistency across various setups.

Further comparisons between M<sup>2</sup>AS measurements and full two-dimensional mass-mobility distributions would be invaluable in enhancing our understanding of the system's performance. Such comparisons would provide a more detailed and comprehensive assessment of how the M<sup>2</sup>AS handles different aerosol types, especially in cases where complex

particle morphologies or size distributions are involved. By comparing the M<sup>2</sup>AS measurements with the full mass-mobility distributions, it would be possible to identify any discrepancies or limitations in the system's ability to accurately characterise aerosols across a broader range of sizes and compositions. Additionally, these comparisons would offer further insights into how well the M<sup>2</sup>AS integrates multiple measurements, such as particle mobility, effective density, and mass, into a unified framework, which could lead to further refinements in its data analysis and interpretation. Ultimately, these studies would help validate the system's versatility and accuracy under various experimental conditions and improve the precision of inversion procedures, making the M<sup>2</sup>AS a more robust tool for aerosol characterisation.

In this thesis, all measurements were performed using a stepped procedure, where the CPMA set-point was adjusted and stabilised before data points were recorded. This approach necessitated a trade-off between measurement time and the number of data points collected. However, the Monte Carlo method used to calculate the CPMA transfer function in this work provides a significant advantage, as it can be directly applied to time-varying scenarios. Moreover, the Monte Carlo method does not require a specific voltage or speed profile, unlike SMPS or Scanning AAC measurements. By scanning the CPMA, measurement times could be shortened whilst also allowing for more data points to be collected per decade of mass, which would likely improve the accuracy of inversion procedures.

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# Appendix A

## Diffusion Charging Theory

### A.1 Calculation of Aerosol-Ion Attachment Coefficient

The theory of Fuchs [49] is commonly used to calculate ion-aerosol attachment coefficients due to electrostatic and diffusive forces in the absence of external electric fields. Fuchs used a limiting sphere model wherein, ionic motion is described by two different physical phenomena in the regions divided by the sphere. Outside of the sphere, continuum mechanics are used and the ion motion is described by diffusion theory. Inside the limiting sphere, ions are assumed to undergo no further collisions with either gas molecules or other ions. Reischl et al. [163] provides an extremely useful summary of Fuchs' work. The collision rate coefficient,  $\beta$ , is defined to quantify the rate of collision between ions and particles, and is given by

$$\beta = \frac{\pi \delta^2 \bar{c}_i \alpha_i \exp\left(\frac{-\phi(i, \delta)}{k_B T}\right)}{1 + \exp\left(\frac{-\phi(i, \delta)}{k_B T}\right) \frac{\delta \bar{c}_i \alpha}{4D_i} \int_0^1 \exp\left(\frac{\phi(i, \delta/x)}{k_B T}\right) dx} \quad (1.01)$$

where

$$\phi(i, r) = \frac{e^2}{4\pi\epsilon_0} \left( \frac{i}{r} - \kappa \frac{a^3}{2r^2(r^2 - a^2)} \right). \quad (1.02)$$

$\bar{c}_i$  is the mean molecular velocity, and  $\pi\delta^2$  is the collisional cross-sectional area, where  $\delta$  is the limiting sphere radius given by

$$\delta = \frac{a^3}{\lambda_i^2} \left( \frac{1 + \lambda_i/a}{5} - \frac{(1 + \lambda_i^2/a^2)(1 + \lambda_i/a)^3}{3} + \frac{2}{15} \left( 1 + \frac{\lambda_i^2}{a^2} \right)^{\frac{5}{2}} \right) \quad (1.03)$$

where  $a$  is the particle radius and  $\lambda_i$  the mean free path of the ion.  $k_B$  and  $T$  are Boltzmann's constant and temperature respectively, whilst  $D_i$  is the ion diffusivity. The electrostatic potential,  $\phi$ , is a function of particle material via the material dielectric constant  $\kappa^1$ , radius,  $a$ , and distance from the centre of the particle,  $r$ . The number and polarity of particle charges,  $i$ , is positive if the ion and particle are of the same polarity.  $\alpha_i$  is the collision probability which represents the fraction of ions emerging from the limiting sphere that actually reach the particle [71].  $\alpha_i$  is calculated as  $\alpha_i = (b_{\min}/\delta)^2$  where  $b_{\min}$  is the minimum collision parameter which is calculated by setting the derivative with respect to  $r$  of the following function to zero,

$$b^2 = r^2 \left( 1 + \frac{2}{3} (\phi(i, \delta) - \phi(i, r)) \right). \quad (1.04)$$

The calculation of ion-aerosol attachment coefficients requires the following ion properties mass,  $m_i$ , electrical mobility  $Z_i$ , diffusion coefficient  $D_i$ , mean thermal velocity  $\bar{c}_i$  and the mean free path of ions  $\lambda_i$ .  $D_i$ ,  $\bar{c}_i$  and  $\lambda_i$  can be calculated from two parameters: ion mobilities and masses. Ion mass and mobility values can be chosen to fit charging measured [197]. However, it is also common to use a single ion property to determine other properties. For the work in Chapter 3, where ion mobility measurements were made, the Steiner mass-mobility relation was used to convert from mobility to mass[186], which is given by

$$m_i = \left( \frac{Z + 0.315}{9.026} \right)^{\frac{-1}{0.318}}. \quad (1.05)$$

$D_i$ ,  $\bar{c}_i$  and  $\lambda_i$  were calculated according to the work of Reischl et al. [163].  $D_i$  is given by the stokes einstein relation

$$D_i = \frac{Z_i}{ek_b T}, \quad (1.06)$$

the mean thermal velocity of the ion can be calculated from

$$\bar{c}_i = \sqrt{\frac{8k_b T}{\pi m_i}} \quad (1.07)$$

and the ionic mean free path can be calculated from

$$\bar{\lambda}_i = \frac{16\sqrt{2}}{3\pi} \frac{D_i}{\bar{c}_i} \left( \frac{M}{m_i + M} \right)^{\frac{1}{2}} \quad (1.08)$$

---

<sup>1</sup>  $\kappa = \frac{\epsilon - 1}{\epsilon + 1}$  where  $\epsilon$  is the material dielectric constant.  $\kappa = 1$  for a perfectly conducting particle

where  $M$  is the mass of the carrier gas. After calculation of the attachment coefficient, a set of population balance equations is solved to determine the charge distribution for a given  $n_i t$  value.

For the case of calculating the unipolar charge distribution on a particle of a given size, in which only ions of a single polarity exist, the following set of population balance equations can be solved once  $\beta$  values have been calculated

$$\frac{dN_0}{dt} = -\beta_0 N_0 n_i \quad (1.09)$$

$$\frac{dN_1}{dt} = \beta_0 N_0 n_i - \beta_1 N_1 n_i \quad (1.10)$$

$$\vdots \quad (1.11)$$

$$\frac{dN_q}{dt} = \beta_{q-1} N_{q-1} n_i - \beta_q N_q n_i. \quad (1.12)$$

Where  $N_q$  is the concentration of particles with  $q$  elementary charges, and  $n_i$  is the ion number concentration (which is assumed constant in the charging region).

## A.2 Numerical Polydisperse Ion and Polydisperse Particle Charging Model

A zero-dimensional model has been implemented in MATLAB to determine how polydisperse ion distributions affect mean charge measurements. The numerical model is a simple 0-dimensional implementation of the model developed by Carsí and Alonso [28], wherein a detailed analysis of heterogeneous ion charging has been performed for the case of a tubular geometry.

Consider a population of polydisperse ions in an environment void of particles whilst also neglecting diffusive and electrostatic losses. The following equation governs the rate of change of ions of bin  $k$

$$\frac{dn_k}{dt} = g_k - n_k \sum_{j=1}^{j=B} \alpha_{kj} \mu_{kj} n_j \quad (1.13)$$

where  $g_k$  is the ion generation rate and  $n_k$  is the number concentration, of ions in bin  $k$ .  $\alpha_{kj}$  is the recombination coefficient between an ion in bin  $k$  and bin  $j$ , it is taken to be the same for all ions, equal to  $1.6 \times 10^{-12} \text{ m}^3 \text{ s}^{-1}$ .  $\mu_{kj}$  is a factor which is 1 if the ions in bins

$k$  and  $j$  are of opposite polarity and 0 if they are of the same polarity.  $B$  is the maximum number of ion bins within the simulation.

Once the ions reach a steady state concentration, the generation rate of ions can be obtained by setting the left-hand side of Equation 1.13 to zero. Resulting in the following for the generation rate of ions in bin  $k$

$$g_{k,0} = n_{k,0} \sum_{j=1}^{j=B} \alpha_{kj} \mu_{kj} n_{j,0} \quad (1.14)$$

where the subscript 0 denotes the quantity evaluated as an initial condition. Once particles are introduced into the domain the following two equations govern the change in the population of ions and particles over time

$$\frac{dn_k}{dt} = g_{k,0} - n_k \sum_{j=1}^{j=k} \alpha_{kj} \mu_{kj} n_j - \sum_{b=1}^{b=M} \sum_{j=q_{\min}}^{j=q_{\max}} n_k \beta_{j \rightarrow j \pm 1} N_{j,b} \quad (1.15)$$

$$\frac{dN_{j,b}}{dt} = \sum_{k=1}^{k=B} n_k \beta_{j-1 \rightarrow j} N_{j-1,b} + \sum_{k=B}^{k=-1} n_k \beta_{j+1 \rightarrow j} N_{j+1,b} - \sum_{k=-B}^{k=-B} n_k \beta_{j \rightarrow j \pm 1} N_{j,b} \quad (1.16)$$

where  $N_{j,b}$  is the particle concentration of a particle with charge  $j$  from polydispersed particle bin  $b$ . In this work, as the particles are monomodal,  $b = 1$ .

In these simulations, it is assumed the positive and negative ion concentrations are equal, even though the integrated concentrations measured using the HRDMA were different. The average charge on a monodisperse particle was obtained by solving the differential equations for sufficient time such that the charge distribution reached a steady state. The charge distribution was then integrated over to obtain the mean charge.

## Appendix B

# High Resolution DMA Calibration and Data Inversion

### B.1 High-Resolution DMA Calibration

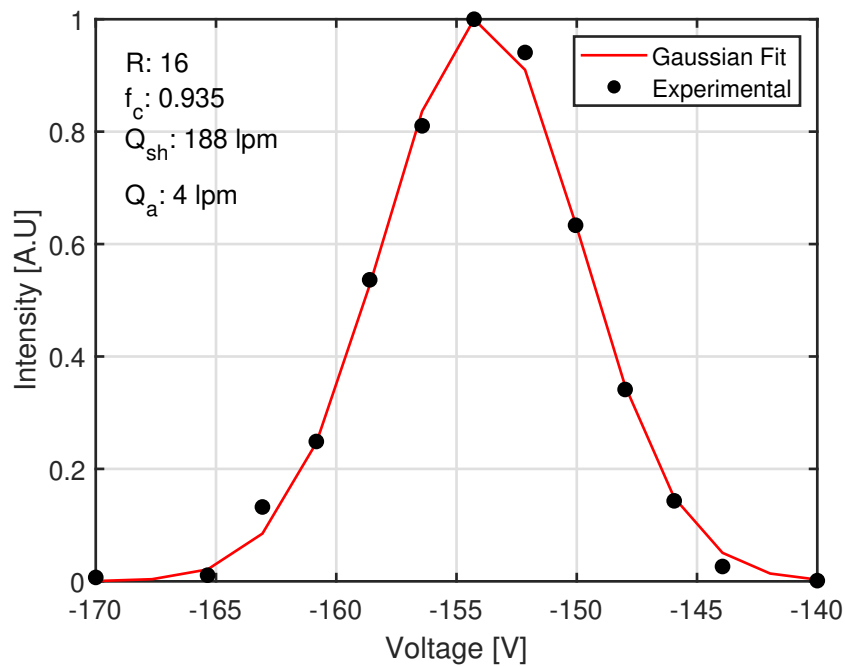


Fig. B.1 Calibration scan of  $\text{THA}^+$ , 1.47 nm molecular ion measured at a sheath flow rate of  $188 \text{ L min}^{-1}$  and aerosol flow rate of  $4 \text{ L min}^{-1}$

To calibrate an aerosol classification instrument a monodisperse particle size standard is often used. Ude and De La Mora [206] demonstrated that the  $\text{THAB}^+$  in air has a

well defined electrical mobility of  $0.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in air. For calibration, the HRDMA was operated with an aerosol flow of  $4 \text{ L min}^{-1}$  and a sheath flow between  $180 \text{ L min}^{-1} \sim 190 \text{ L min}^{-1}$ . A 2 mmol solution of THAB in methanol was electrosprayed by a TSI electrospray operating a flow rate of  $1.2 \text{ L min}^{-1}$  and a voltage of 1.7 kV. Downstream of the electrospray dried make-up air (confirmed with an RH sensor) was added. It is crucial that the air is dried sufficiently so that the THAB<sup>+</sup> ions do not cluster with water molecules thereby changing their electrical mobility. An example calibration scan is shown in Figure B.1. A Gaussian was fit to the data to determine the calibration factor  $k$  which converts the voltage set-point of the DMA to electrical mobility, and the resolution of the HRDMA at a size of 1.47 nm. The calibration factor was found to be 0.935 of the theoretical value given by  $\frac{Q_{\text{sh}} \ln(\frac{r_2}{r_1})}{2\pi L}$ . The resolution, given by the full width at half maximum, was 16.

## B.2 High-Resolution DMA Data Inversion

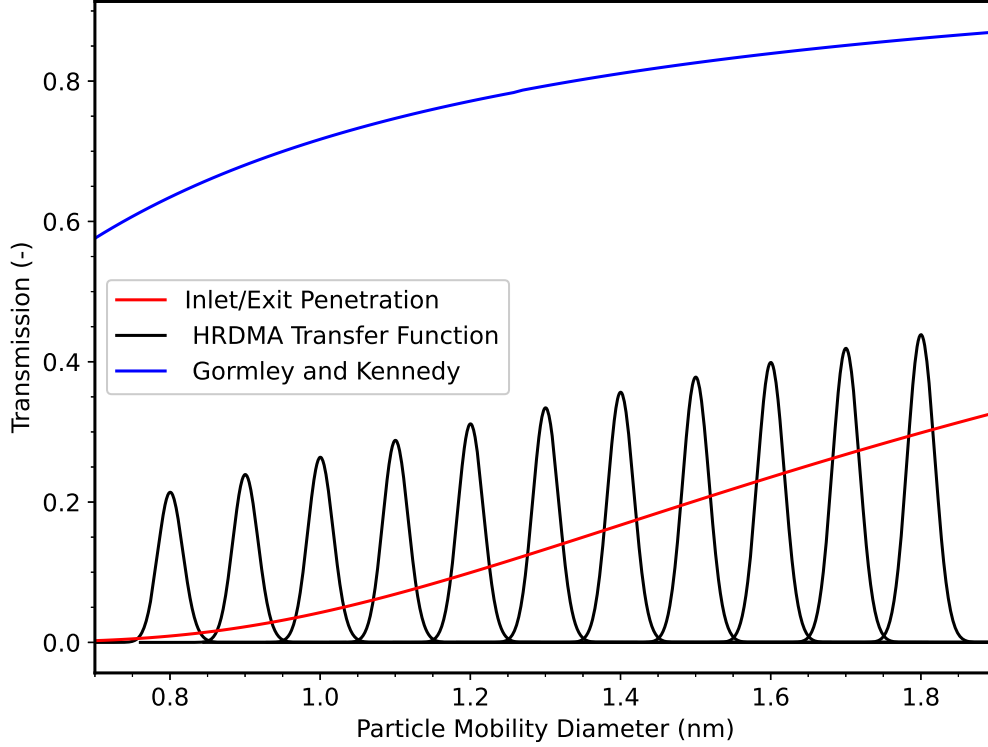


Fig. B.2 Transmission as a function of particle mobility diameter.

Here, the process of inversion used to convert the raw HRDMA concentration measurements into a distribution is described. It should be noted that the inversion method is a one-to-one linear inversion method (sometimes referred to as a point-to-point inversion). This method makes several assumptions about the aerosol distribution and transfer function width which are not necessarily made in other inversion methods.

The particle number concentration ( $N_m$ ) measured by an electrometer downstream of a HRDMA operating at mobility set-point  $Z^*$  is [190]:

$$N_m(Z^*) = \int \eta(Z^*) f_c(Z^*) P_{\text{Tube}} \lambda_{\text{DMA}} \Omega(V, \tilde{Z}) N(Z) dZ \quad (2.01)$$

where  $\eta(Z^*)$  is the counting efficiency of the electrometer,  $P_{\text{Tube}}$  is the penetration of particles through any tubing lengths between the particle source and counting device (excluding any effective lengths of the DMA),  $P_{\text{DMA}}$  the inlet and exit losses of the HRDMA,

$f_c(Z^*)$  the charge fraction of the aerosol and  $\Omega(V, \tilde{Z})$  the diffusing transfer function of the DMA.  $N(Z)$  is the desired distribution function.

Tube penetration is calculated using the classical formula experimentally determined for laminar flow in a pipe [59] as follows

$$P_{\text{Tube}} = 1 - 2.56x^{\frac{2}{3}} + 1.2x + 0.177x^{\frac{4}{3}} \quad (2.02)$$

$$P_{\text{Tube}} = 0.819 \exp(-3.657x) + 0.097 \exp(-22.3x) + 0.032 \exp(-57x). \quad (2.03)$$

where

$$x = \frac{\pi DL}{Q}. \quad (2.04)$$

$D$  is the diffusion coefficient,  $L$  the length of tubing within the system which includes tubing between the particle charger and HRDMA inlet as well as tubing between the HRDMA outlet and the electrometer and  $Q$  is the sample flow rate. For the work here a total of length of approximately 20 cm was used between the inlet and exit of the DMA.

The diffusing DMA transfer function,  $\Omega(V, \tilde{Z})$  is given by [190]

$$\Omega(V, \tilde{Z}) = \frac{\sigma}{\sqrt{2}\beta(1-\delta)} \cdot \left[ \operatorname{erf}\left(\frac{\tilde{Z} - (1+\beta)}{\sqrt{2}\sigma}\right) + \operatorname{erf}\left(\frac{\tilde{Z} - (1-\beta)}{\sqrt{2}\sigma}\right) + \operatorname{erf}\left(\frac{\tilde{Z} - (1+\beta\delta)}{\sqrt{2}\sigma}\right) - \operatorname{erf}\left(\frac{\tilde{Z} - (1-\beta\delta)}{\sqrt{2}\sigma}\right) \right] \quad (2.05)$$

$\tilde{Z} = Z/Z^*$  is the non-dimensional electrical mobility normalised by the mobility set-point  $Z^*$ ,  $\beta$  is the aerosol to sheath flow ratio, and  $\delta$  characterizes the difference between the aerosol inlet flow rate and the classified aerosol flow, this is taken to be zero (i.e. balanced flows) within this work.  $\operatorname{erf}()$  denotes the error function.  $\sigma$  is a non-dimensional broadening parameter given by

$$\sigma^2 = \frac{Gk_b T \tilde{Z}}{eV^*} \quad (2.06)$$

where  $G$  is a non-dimensional geometry factor,  $k_b$  is the Boltzmann Constant,  $T$  temperature,  $e$  the electron charge and  $V^*$  the operating voltage of the DMA. The theoretical transfer function strictly details the probability a particle exits the classification region of the DMA for a given set of operating conditions, the penetration through the inlet and exit regions as

well as any other non-idealities also need to be taken into account. The penetration through a Half-mini DMA has been experimentally determined by Cai et al. [27] and is given by

$$\lambda_{\text{DMA}} = 0.82 \cdot \exp\left(\frac{-2.57}{d_m^2}\right) \cdot \exp\left(\frac{-1.56}{d_m \cdot Q_a}\right). \quad (2.07)$$

Equation 2.07 should be viewed as an approximation of the non-idealities within the DMA used due to the significant uncertainties in measurement at small sizes.

Equations 2.02, 2.05 and 2.07 require an input of the diffusion coefficient and mobility diameter of a particle. A conversion from electrical mobility to mobility diameter is therefore required. In this work, the conventional Stokes-Milikan relationship of electrical mobility to particle size is used

$$Z_p = \frac{neC_c(d_m)}{3\pi\mu d_m}. \quad (2.08)$$

The Cunningham slip correction factor can be estimated from the following correlation developed by [93]:

$$C_c(d_m) = 1 + \frac{\lambda}{d_m} \left( \alpha_c + \beta_c \exp\left(\frac{-\gamma_c d_m}{\lambda}\right) \right) \quad (2.09)$$

where  $\alpha_c = 2.33$ ,  $\beta_c = 0.966$  and  $\gamma_c = 0.4985$ . The mean free path,  $\lambda$  and viscosity  $\mu$  of the surrounding gas can also be estimated from the same source [93]:

$$\lambda = \lambda_0 \left(\frac{T}{T_0}\right)^2 \left(\frac{P_0}{P}\right) \left(\frac{T_0 + S}{T + S}\right) \quad (2.10)$$

and

$$\mu = \mu_0 \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \left(\frac{T_0 + S}{T + S}\right) \quad (2.11)$$

where  $\lambda_0$  reference value of the air mean free path taken as 67.3 nm,  $\mu_0$  is the air viscosity reference given by  $1.83245 \times 10^{-5}$  Pa s,  $T$  is the air temperature in the classifier,  $T_0$  is the reference temperature of 296.15 K,  $P$  is the air pressure in the classifier,  $P_0$  is the reference pressure of 101325 Pa and  $S$  is the Sutherland constant for air which is 110.4 K.

The various functions involved in the inversion for a sample flow rate of  $4 \text{ L min}^{-1}$  and sheath flow rate of  $180 \text{ L min}^{-1}$  are plotted in Figure B.2. Having established the relationships and forms of the variables used in Equation 2.01 the integration can be simplified by assuming that the counting efficiency, particle penetrations and number concentration are constant over the narrow width of the DMA transfer function and therefore they are considered constants within the integration. The assumption of constant counting efficiency, particle

penetrations and number concentration over the transfer function is a good approximation for particles/ions of the size of a THAB ion as the resolution is high, as discussed within the calibration section. This can also be seen in Figure B.2 in which both the tube penetration and inlet and exit penetrations are relatively flat over the width of the DMA transfer function. All ions are considered to have a single charge such that  $f_c(Z^*) = 1$ . Converting to logarithmic space by noting that

$$N(Z) = \frac{dN}{dZ} = \frac{dN}{d \log Z} \frac{d \log Z}{dZ} = \frac{dN}{d \log Z} \frac{1}{\ln(10)} \quad (2.12)$$

and substituting into Equation 2.01. The spectral density for each electrical mobility set-point  $Z^*$  is given by

$$\left. \frac{dN}{d \log Z} \right|_{Z^*} = \frac{N_m \cdot \ln(10)}{\eta|_{d_m^*} P_{\text{Tube}}|_{d_m^*} P_{\text{DMA}}|_{d_m^*} \int \frac{\Omega(Z, Z^*)}{Z} dZ} \quad (2.13)$$

Although not done in this work, this can be readily converted into mobility diameter space by noting that

$$\frac{dN}{d \log d_m} = \frac{dN}{d \log Z} \cdot \frac{d \log Z}{d \log d_m} \quad (2.14)$$

where

$$\frac{d \log Z}{d \log d_m} = 2 + \frac{-1 + \gamma_c \beta_c \exp\left(-\frac{\gamma_c d_m}{\lambda}\right)}{C_c(d_m)}. \quad (2.15)$$

## Appendix C

# Additional Measurements and Considerations for Calibration of the MSE

### C.1 Calibration of MSE using a DMA: Effect of DMA Resolution and Charging Mechanism

Figures C.1a and b show the effect of upstream DMA resolution on the electrical mobility determined by the MSE when charging the aerosol with a bipolar charger (Figure C.1a) and a unipolar charger (Figure C.1b) before electrical mobility classification with the DMA. Upstream DMA resolution,  $R$  is defined as the sheath to aerosol flow rate, operating the DMA with balanced flows. Accurate calibration of the MSE is imperative to obtaining accurate measurements of effective density. As can be seen in both figures, running with low resolutions ( $R = 5$ ) can lead to errors greater than 4% between the upstream DMA electrical mobility and the MSE calculated electrical mobility. However, as the resolution increases and the resulting electrical mobility distribution narrows, these errors generally reduce to less than 1%. However, extra care must be taken when using a unipolar charger due to the narrow electrical distribution produced (Figure C.1d). The electrical mobility distribution of particles exiting a unipolar charger is extremely narrow because the particle charge scales approximately with particle mobility diameter ( $q \sim d_m$ ), and therefore, the electrical mobility is only weakly dependent on the particle size through the Cunningham Slip Correction Factor. When selecting from the left-hand tail of the distribution, significant errors can occur due to the sharply changing concentrations over the width of the transfer function, regardless of the resolution. It is therefore advised to calibrate the MSE using a high upstream DMA

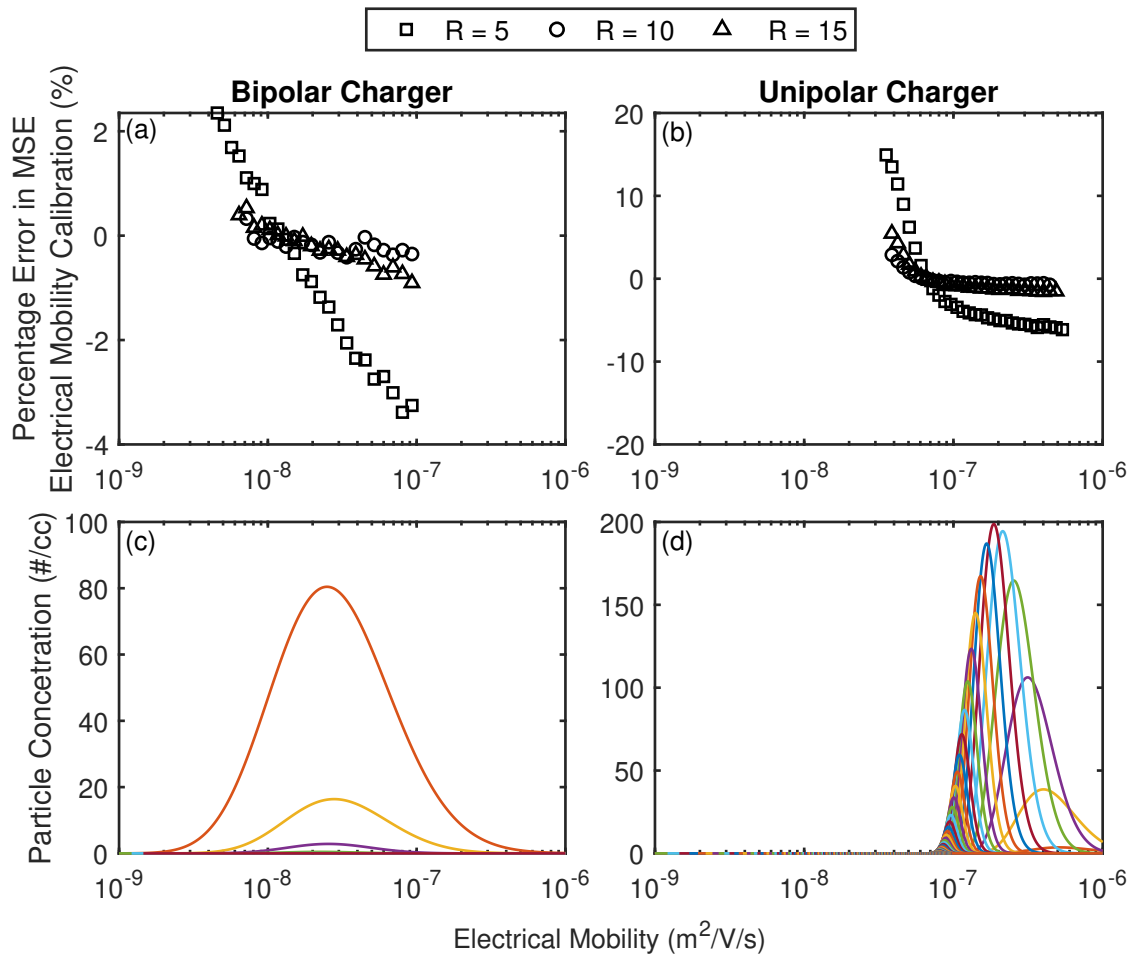


Fig. C.1 Numerical results indicating errors that can occur when calibrating an MSE with a DMA. Figures (a) and (b) show the error in the MSE-determined electrical mobility by balancing the incoming currents relative to the upstream DMA set-point. Figures (c) and (d) show the corresponding electrical mobility distribution of Ammonium Sulphate when using a bipolar charger and unipolar charger, respectively. Coloured lines correspond to different charge states.

resolution ( $R \geq 10$ ) and ensure that particles are not selected from the left-hand tail of the electrical mobility distribution.

## C.2 Single Charge Calibration of Electrometer and CPC

Figure C.2 shows the calibration of the electrometer and CPC using singly charged particles. Singly charged particles were generated by overlapping the transfer functions of tandem classifiers, which ensures multiply charged particles are eliminated from the sample [224].

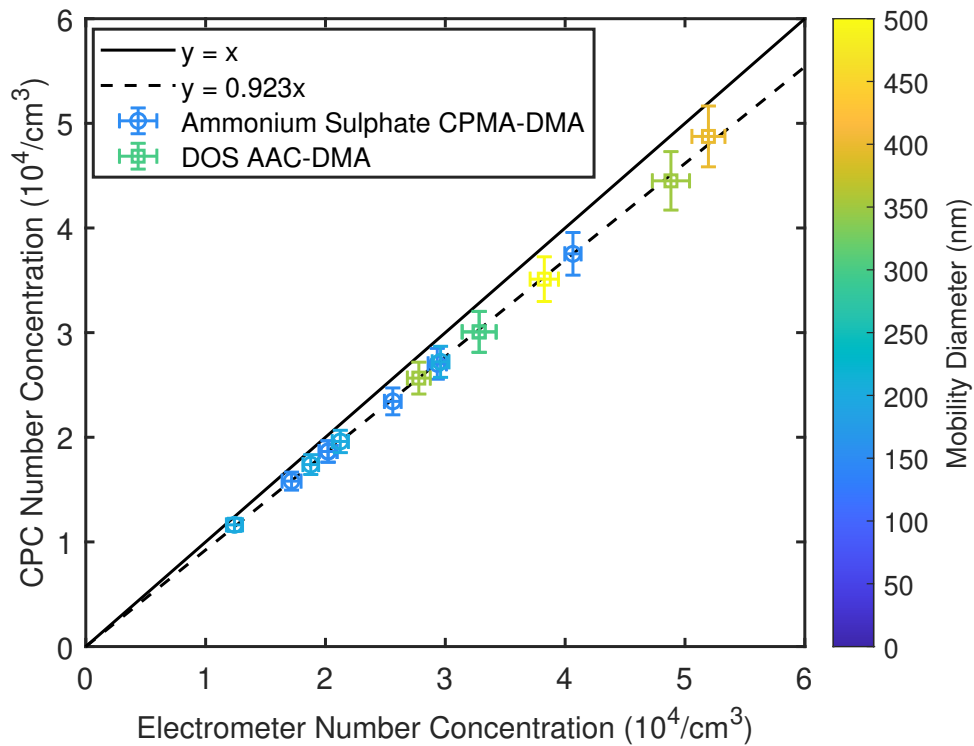


Fig. C.2 Calibration of CPC to electrometer counting ratio using singly charged particles generated from tandem classification. Error bars represent combined Type A and B uncertainties. Type A uncertainties were taken as  $1\sigma$  over the measurement duration in the electrometer current and CPC concentration measurement, and Type B uncertainties equate to 2 fA for the electrometer current and 5% for the CPC concentration.

Singly charged Ammonium Sulphate particles were generated using a tandem CPMA-DMA, whilst singly charged DOS particles were generated using a tandem AAC-DMA at a range of particle diameters and concentrations. The CPC used in the effective density measurements was found to under-count relative to the MSE by 8.3%. Therefore, a correction factor was implemented to account for this disparity in counting.

### C.3 Particle Losses within the Mobility Separator

An experimental set-up similar to that used in determining the MSE transfer function was used to determine particle losses within the MSE. However, instead of selecting particles with a DMA, particles were selected using an AAC. The total current transmitted through the MSE was determined by summing the currents between the high and low mobility electrometers. Here the MSE was operated with its PID control enabled in order to balance

the current outputs between the two outlets. The total current downstream of the AAC was then measured by bypassing the MSE classifier and sampling directly with the low-mobility electrometer. The ratio of these two measurements provided a transmission factor through the MSE, which was determined over a wide size range from 30 nm to 4000 nm.

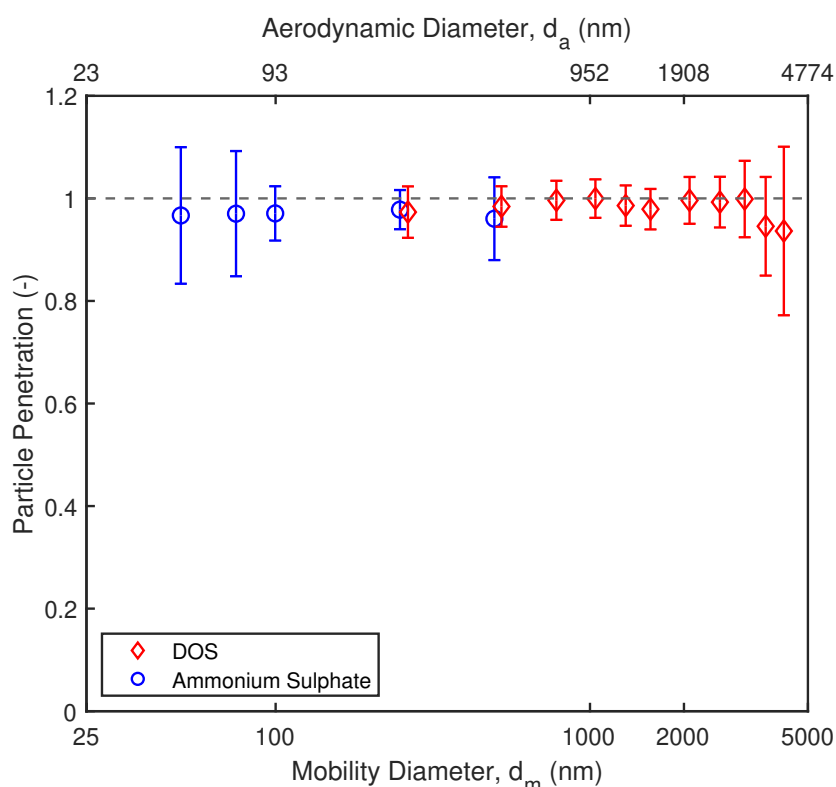


Fig. C.3 Experimentally determined losses within the MSE. The top aerodynamic axis is calculated from the mobility diameter based on DOS particles, which are spherical and have an effective density of  $913 \text{ kg m}^{-3}$ . Therefore, the top aerodynamic axis only corresponds to results for the DOS aerosol, indicated by red diamonds. Uncertainty has been determined using both Type A and B uncertainties. Type A uncertainties are considered to be  $1\sigma$  over the duration of a measurement sample (180 s), and Type B are considered to be equal to either 2% of the electrometer current or 1 fA, whichever is greater.

Attaining 100% transmission efficiency through the MSE is imperative to the combined operation of the CPC and MSE. Determining the mean charge per particle assumes that both the CPC and electrometers incur no loss within inlets and exits and within sampling tubing lengths between the two instruments when the sample flow is split. Furthermore, the calculation of mean charge assumes no bias in splitting the flow between the instruments. If particles are lost to the walls unevenly between the two instruments, then the average charge measurement will be incorrect. Three main loss mechanisms are pertinent to the MSE: diffusion, impaction and electrophoretic loss. Diffusion losses are the dominant loss

mechanism for particles smaller than 100 nm in mobility size, whereas impaction dominates for larger particles, although this depends on particle inertia. Electrophoretic losses can affect all particle sizes and depend on the number concentration and charge distribution of the aerosol entering the MSE [4]. The particle penetration through the MSE as a function of size is shown in Figure C.3. There are minimal losses within the MSE owing to its small classification length and gradual changes in flow direction. Uncertainties are larger at the smallest and largest sizes due to reduced current signals.

A word of caution has to be made when utilising the MSE with different CPCs. Typically, all CPCs have a flat counting efficiency close to 1 between 100 nm and 1  $\mu\text{m}$ . However, the counting efficiency outside of this size range is dependent on CPC type and particle composition [212, 112]. Therefore, corrections for calculation of the mean charge may be required on a case-by-case basis depending on the CPC used.

## C.4 The Effect of Field Charging on Effective Density Measurements

Field charging occurs in the presence of an external electric field as ions travel along electrical field lines and collide with the particle, transferring their charge to it [70]. The charge acquired by a particle undergoing field charging is proportional to the square of its diameter and, therefore, is dominant for larger particle sizes. The limiting sphere model proposed by Fuchs [49] does not include the effect of external electric fields. However, Lawless [101] proposed a model including field and diffusion charging for particles within the continuum regime.

The commercial UDAC, used within the experimental validation in this work, operates with a square wave voltage of 400 V which is applied in an annular gap with inner and outer radii of 10 mm and 45 mm, respectively. This provides an average electric field strength of approximately  $10 \text{ kV m}^{-1}$ .

As shown in Figure C.4, the effect of field charging across most of the size range is negligible for both classification methods. However, at the very largest sizes, when using the CPMA as the upstream classifier, there is a sharper increase in the effective density relative to the true effective density when an electric field strength of  $100 \text{ kV m}^{-1}$  is applied within the charging zone. The extent to which field charging impacts measurements, therefore, needs to be evaluated on a charger-by-charger basis, specifically when measuring particles greater than  $\sim 2 \mu\text{m}$ .

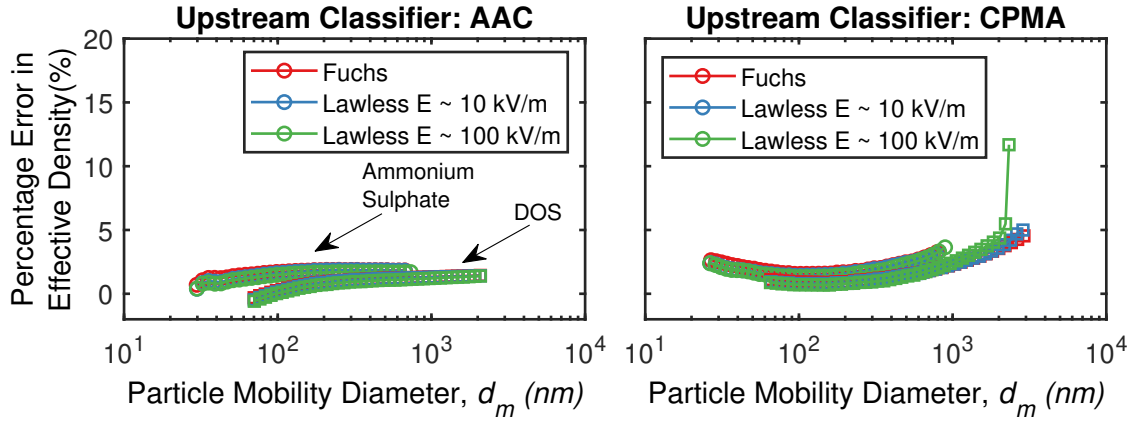


Fig. C.4 Effect of Field Charging on the measurement of effective density using tandem MSE systems. Shown is the comparison to Fuchs' theory to Lawless with a low electric field strength, as in the commercial UDAC, and a high field strength

## C.5 Uncertainty Analysis for an UDAC-AAC-MSE-CPC System

In calculating the total uncertainty in measurements, two types of uncertainties should be considered: precision uncertainty and bias uncertainty. The precision uncertainty (Type A) in this work is taken as the standard deviation ( $1\sigma$ ) in measurements over a measurement duration, which were 30 s - 180 s depending on the measurement. Bias uncertainty (Type B) is the instrument's error in reading a measurement's true value. When a particle measurement depends on several different independent variables such as  $f(x_1, x_2, \dots)$ , propagation of uncertainty can be used as follows

$$\varepsilon_x = \sqrt{\left(u_{x_1} \frac{\partial f}{\partial x_1}\right)^2 + \left(u_{x_2} \frac{\partial f}{\partial x_2}\right)^2 + \left(u_{x_3} \frac{\partial f}{\partial x_3}\right)^2 + \dots} \quad (3.01)$$

where  $u$  denotes the uncertainty in the independent variable.

Before applying Equation S3.01 to the MSE calculation of electrical mobility,  $Z_p = \frac{Q_a \ln(\frac{r_2}{r_1})}{4\pi LV}$ , it is assumed that the logarithmic ratio of the radii in the MSE classifier can be approximated as  $\frac{r_2}{r_1} - 1$ . This is a reasonable approximation owing to the small gap within the classifier. The uncertainty in electrical mobility is then given by

$$\frac{u_{Z_p}}{Z_p} = \sqrt{\left(\frac{u_{Q_a}}{Q_a}\right)^2 + \left(\frac{u_V}{V}\right)^2 + \left(\frac{u_L}{L}\right)^2 + \left(\frac{u_r^2 \left(\left(\frac{r_2}{r_1}\right)^2 + 1\right)}{(r_2 - r_1)^2}\right)} \quad (3.02)$$

Assuming an uncertainty of 1% in voltage, 3.3% in classifier length, 1% in flow rate and a 25  $\mu$ m uncertainty in both the inner and outer classifier radius, the uncertainty in electrical mobility is 4%.

The uncertainty in mean charge depends on the uncertainty of the CPC count and uncertainty within the electrometer reading. As the mean charge is linearly dependent on all variables, it is given by the sum in quadrature of the corresponding variables; the error in electron charge is negligible and is not included

$$\frac{u_{\bar{q}}}{\bar{q}} = \sqrt{\left(\frac{u_{Q_a}}{Q_a}\right)^2 + \left(\frac{u_i}{i}\right)^2 + \left(\frac{u_N}{N}\right)^2}. \quad (3.03)$$

The uncertainty in electrometer current is dependent on the magnitude of the current. Here, an uncertainty of 2 fA or 2%, whichever is greater is assumed. The uncertainty in CPC count was taken to be 5% as per manufacturer specifications.

From the measures of mean charge and electrical mobility, the particle mobility diameter can be calculated with the following uncertainty

$$\frac{u_{d_m}}{d_m} = \sqrt{\left(\frac{u_{Z_p}}{Z_p}\right)^2 + \left(\frac{u_{\mu}}{\mu}\right)^2 + \left(\frac{u_{C_c}}{C_c}\right)^2 + \left(\frac{u_{\bar{q}}}{\bar{q}}\right)^2} \quad (3.04)$$

The uncertainty in viscosity is 0.5% and uncertainty in Cunningham slip 2.5% [95], so the total uncertainty in mobility diameter calculated from the MSE and CPC combination is  $\sim 7.3\%$ . Note that this is just over twice the uncertainty in mobility diameter measured with a conventional DMA [96]. The dominating uncertainty in this measurement is the uncertainty in the particle charge. Effective density uncertainty can be calculated using the same method as Tavakoli and Olfert [195]. If the uncertainty in the electrometer is 2% and the uncertainty in aerodynamic size is 4.3% [195], this gives an uncertainty of 18% in effective density.



## Appendix D

# M<sup>2</sup>AS Trasnsfer Function and Uncertainty

### D.1 Monte Carlo Simulation of the CPMA classification section

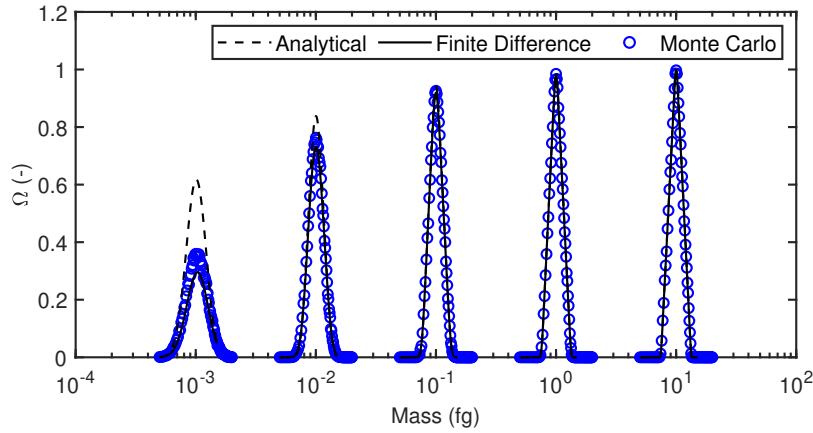


Fig. D.1 Validation of Monte Carlo method to determine the CPMA transfer function. Validation was performed for singly charged particles using a constant resolution,  $R_m = 3$ , and for spherical particles of a constant density,  $1000 \text{ kg m}^{-3}$ . Also shown are the analytical and finite difference methods described by Sipkens et al. [182] and Olfert and Collings [145].

Here, a Monte Carlo method is proposed to determine the transfer function of the CPMA rather than using the analytical method of Sipkens et al. [182]. The use of a Monte Carlo model, rather than the analytical model of Sipkens et al. [182], is motivated by future extensions of this work, which will explore scenarios where the CPMA is operated with a

time-varying angular speed and voltage profile. The proposed Monte Carlo model is readily adaptable to time-varying scenarios, unlike current analytical methods. Hagwood et al. [62] implemented a Monte Carlo model for the now more commonly known Aerosol Particle Mass Analyser, as well as for the DMA [63]. The Monte Carlo model used here is similar to Hagwood's work, although there are some differences in the assumptions made and the classifier used.

The model begins by describing the equations of motion of a particle within the CPMA. The CPMA consists of two concentric cylinders rotating around their axis with a potential difference between them. The centrifugal force field induces a centrifugal force ( $F_C$ ) on a particle proportional to its mass at a radial position  $r$ :

$$F_C = m\omega^2 r = \frac{mv_\theta^2}{r}. \quad (4.01)$$

The inner cylinder of the CPMA rotates slightly faster than the outer cylinder to maximise particle transmission [145, 182]. The azimuthal velocity distribution is given by [146]:

$$v_\theta = \omega_1 r \frac{\hat{r}^2 - \hat{\omega}}{\hat{r}^2 - 1} + \frac{\omega_1 r_1^2}{r} \frac{\hat{\omega}^2 - 1}{\hat{r}^2 - 1} = \alpha r + \frac{\beta}{r}, \quad (4.02)$$

where  $\omega_1$  is the rotational speed of the inner electrode,  $\hat{\omega} = \omega_2/\omega_1$  is the ratio of the rotational speeds of the outer to the inner electrode which is equal to 32/33 for the CPMA.  $\hat{r} = r_1/r_2$  is the ratio of the inner to outer electrode radius and  $\alpha$  and  $\beta$  are defined implicitly above.

The electrostatic force on a particle holding  $q$  elementary charges due to the applied voltage is given by:

$$F_E = \frac{qeV}{r \ln(\frac{r_2}{r_1})}. \quad (4.03)$$

A drag force from the surrounding gas molecules impedes the particle's motion in the radial direction:

$$F_D = \frac{1}{B} \frac{dr}{dt}, \quad (4.04)$$

where  $B$  is the mobility of the particle and  $dr/dt$  is the radial velocity of the particle. Applying Newton's law of motion in the radial direction and neglecting the radial acceleration of the particle due to the particle's short relaxation time compared to its residence time within the CPMA, the differential equation for the radial trajectory is:

$$\frac{dr}{dt} = B \left[ m \left( \alpha^2 r + \frac{2\alpha\beta}{r} + \frac{\beta^2}{r^3} \right) - \frac{qeV}{r \ln(\frac{r_2}{r_1})} \right]. \quad (4.05)$$

Axial motion in the  $x$  direction follows a laminar parabolic velocity profile:

$$\frac{dx}{dt} = \frac{3\bar{u}}{2} \left( 1 - \frac{(r-r_c)^2}{\delta^2} \right), \quad (4.06)$$

where  $\bar{u}$  is the average fluid velocity and  $\delta$  is half the gap width,  $(r_2 - r_1)/2$ .

In typical Monte Carlo simulations of aerosol classifiers, the time step must be sufficiently small for the initial radial position to accurately evaluate the forces on the particle. However, smaller time steps increase simulation time. Here, the model integrates along the particle's path, allowing for larger integration steps with minimal accuracy loss. To simplify the complex integration arising from Equation 4.05, a Taylor Expansion is applied about the centre of the gap as in Sipkens et al. [182]:

$$\frac{dr}{dt} \approx C_3 + C_4(r - r_c), \quad (4.07)$$

where

$$C_3 = B \left( m\alpha^2 r_c + m\frac{2\alpha\beta}{r_c} + m\frac{\beta^2}{r_c^3} - \frac{qeV}{r_c \ln(\frac{r_2}{r_1})} \right) \quad (4.08)$$

and

$$C_4 = B \left( m\alpha^2 - m\frac{2\alpha\beta}{r_c^2} - m\frac{3\beta^2}{r_c^4} - \frac{qeV}{r_c^2 \ln(\frac{r_2}{r_1})} \right). \quad (4.09)$$

This expression is then integrated, assuming constant radial velocity over the time step, to yield:

$$r = r_c + \frac{1}{C_4} [\gamma \exp(C_4(t - t_0)) - C_3], \quad (4.10)$$

where

$$\gamma = C_3 + C_4(r_0 - r_c). \quad (4.11)$$

Equation 4.10 is substituted into Equation 4.06 and integrated to determine the axial position:

$$x = \frac{3\bar{u}}{2\delta^2} \left[ \left( \delta^2 - \frac{C_3^2}{C_4^2} \right) (t - t_0) + \frac{2C_3\gamma}{C_4^3} (\exp(C_4(t - t_0)) - 1) - \frac{\gamma^2}{2C_4^3} (\exp(2C_4(t - t_0)) - 1) \right] + x_0. \quad (4.12)$$

A diffusion term is included in the radial direction, given by:

$$r_B \sim \mathcal{N}(0, \sqrt{2D\Delta t}), \quad (4.13)$$

where  $\mathcal{N}(0, \sqrt{2D\Delta t})$  is the normal distribution with mean 0 and standard deviation equal to the root-mean-square net displacement [70]. For deconvolution of experimental measurements, the diffusion term is omitted as corrections for CPMA losses are applied using Naseri et al. [133], as discussed in Chapter 7.

The validation of the Monte Carlo simulation of the classification region of the CPMA was performed using singly charged particles to enable a direct comparison with the analytical form of the diffusing transfer function calculated using the method of Sipkens et al. [182]. A key consideration in the simulation is the choice of integration time step. Figure D.2 demonstrates the impact of the integration time step on the Monte Carlo solution. As anticipated, the discrepancy between the Monte Carlo and analytical solutions decreases as the integration time step is reduced. At a time step of 0.1 s, the error between the two methods is less than 2.5%. Therefore, this time step was used throughout the remainder of this work to balance accuracy with computational efficiency.

The Monte Carlo method was validated for other particle sizes, and excellent agreement was observed between the Monte Carlo simulation and the analytical method for non-diffusing particles, as shown in Figure D.1. However, for more diffusive particles, the analytical method underestimates diffusive losses. This discrepancy is attributed to the assumptions of plug flow and the neglect of particles diffusing to more distant streamlines as streamlines converge within the CPMA [182, 162]. Figure D.1 also includes the transfer function determined using a Finite Difference method. For diffusing particles, the Finite Difference method provides a closer match to the Monte Carlo simulation than the analytical method.

## D.2 Generation of the Inversion Kernel of the Steady State M<sup>2</sup>AS

Typical Monte Carlo simulations of aerosol classifiers simulate the trajectory of particles with a single property, such as mass-to-charge ratio or particle mass in the case of the CPMA,

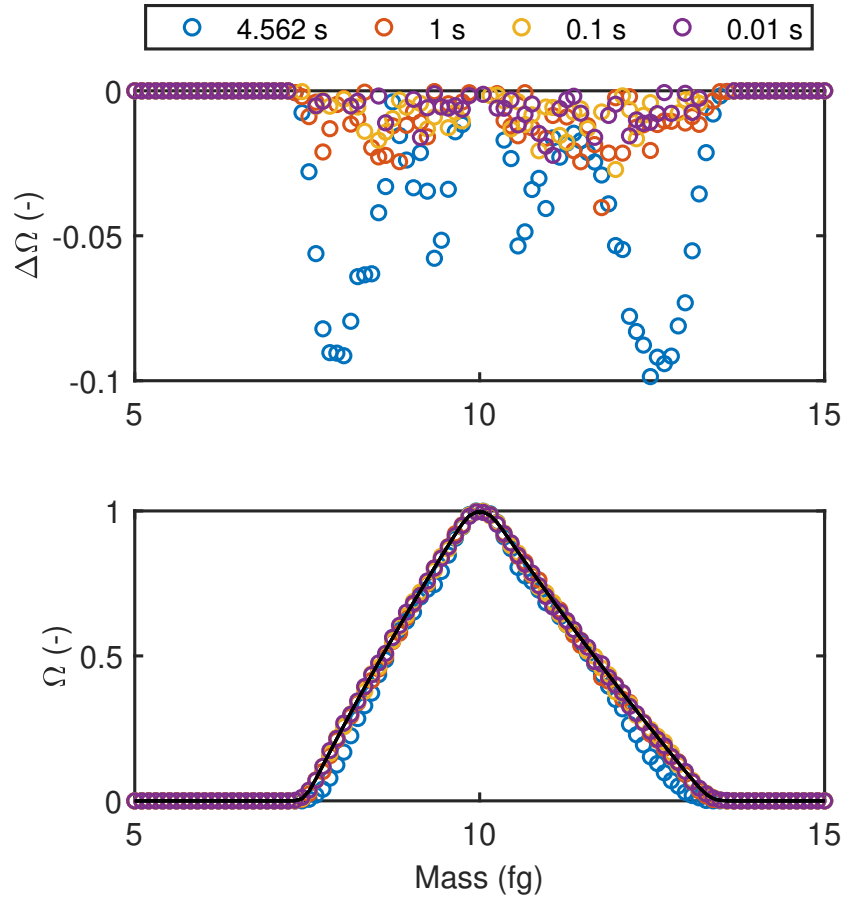


Fig. D.2 The effect of Monte Carlo Integration Time Step. The top Figure shows the relative difference between the Monte Carlo and Analytical transfer function solutions. The bottom figure shows the transfer functions. Legend indicates the integration time step,  $\Delta t$ . The largest integration time step chosen is equal to the average transit time of particles through the CPMA, assuming a volumetric flow rate of  $1 \text{ L min}^{-1}$ .

for given classifier conditions including flow rates, voltages, and rotational speeds [63, 62]. During the simulation, particles of a single mass are advanced in time according to their equation of motion within the classifier, with a check at each time step to determine whether the particle remains within the classification bounds. This process is repeated multiple times, recording the fraction of particles of a given mass successfully transmitted through the classifier. The particle mass is then incremented, and the simulation is repeated for different masses. This approach validated the Monte Carlo method in Figure D.1. However, iteratively computing each particle mass is extremely time-consuming, so a slightly modified approach is used within the M<sup>2</sup>AS Monte Carlo scheme.

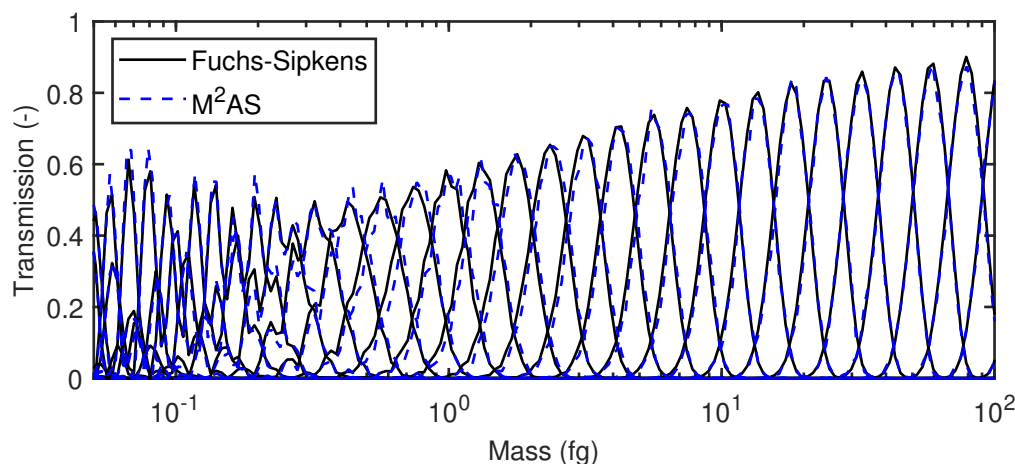


Fig. D.3 Comparison of the full system kernel for the M<sup>2</sup>AS compared to that generated using the analytical charge distribution of Fuchs [49] and analytical form of CPMA transfer function ([182]). To the charge distribution in this, the M<sup>2</sup>AS kernel is approximated by fitting a Gaussian distribution to the model of Fuchs', and the CPMA transfer function is calculated using Monte Carlo methods as outlined in the text.

An initial mass vector is created by randomly sampling 50,000 particles per decade of mass uniformly between the measured mass limits of a M<sup>2</sup>AS measurement. Corresponding mobility diameters are calculated using Equation 7.02, and the corresponding charges are sampled randomly from the Gaussian distribution given by Equation 6.21. These three parameters—mass, charge, and mobility—provide a complete description of particle motion through the CPMA when combined with speed, voltage set-points, and flow rate. Throughout this work, the CPMA is operated in stepped mode, where speeds and voltages are steady for each set-point (i.e. time-invariant). Consequently, only the exit condition of a particle is of interest, not the time of exit. Scenarios involving time-varying speed and voltage profiles (i.e. scanning CPMA) should be explored in future work.

To reduce computational time, the bounds of the Monte Carlo simulation are narrowed before simulation. Estimates of the upper and lower transmitted masses for a given CPMA set-point are calculated using the method of Reavell et al. [162]. These mass limits are then used to truncate the initial mass vector, ensuring only a relevant portion is simulated for each CPMA condition. A 50% margin of error is applied to the estimated mass limits to prevent artificial truncation. For each CPMA set-point, particle trajectories are simulated using the boxed vector of particles. At the CPMA inlet, particles are assigned random radial starting coordinates between  $r_1$  and  $r_2$ , weighted by the parabolic velocity profile given in Equation 4.06. During each time interval  $\Delta t$ , particles are advanced radially and axially according to Equations 4.10 and 4.12. If a particle's motion causes it to collide with either the inner or

outer cylinder of the CPMA (i.e.  $r \leq r_1$  or  $r \geq r_2$ ) while its axial coordinate is less than the length of the classifier,  $L$ , the particle is deemed lost to the wall, and its motion ceases. If the particle axial coordinate exceeds  $L$  while remaining within the radial confines of the classifier, it is flagged as counted. Therefore, for a given input mass vector (and corresponding charge and mobility diameter vectors), an output vector of 0s and 1s is generated, indicating whether each particle is lost or transmitted.

Referring to Equation 6.10, the discretised number-weighted mass distribution  $n(m_j)$ , which is the desired quantity, is evaluated at points  $m_j$ . These points are specified by setting the number of mass classes per decade between the lower and upper mass limits of the M<sup>2</sup>AS measurement. Throughout this work, 64 mass bins per decade were used. For each CPMA set-point, the transfer probability of particles within a given mass bin,  $K(m_j)\Delta m_j$ , is calculated as the ratio of the number of particles exiting the CPMA in that bin to the initial number of particles in the bin. An example of the M<sup>2</sup>AS kernel, calculated using this method, is compared to the analytical functions of Fuchs [49] and Sipkens et al. [182] in Figure D.3. The kernel calculated using the outlined procedure (dashed blue line in Figure D.3) shows good agreement with the kernel calculated using the complete charge distribution and the analytical form of the CPMA transfer function (solid black line), with minor differences due to approximations of the charge distribution as Gaussian as assumed in the M<sup>2</sup>AS.

### D.3 Uncertainty Analysis for average M<sup>2</sup>AS measurements

The uncertainty in M<sup>2</sup>AS measurements follows similarly to those for the UDAC-AAC-MSE-CPC system discussed in Appendix C.5. The precision uncertainty (Type A) in M<sup>2</sup>AS measurements is taken as the standard deviation ( $1\sigma$ ) in the 10 s measurement at each CPMA set-point. Bias uncertainty (Type B) is the instrument's error in reading a measurement's true value. The uncertainties in electrical mobility, mean charge, and average mobility diameter are the same as detailed in section C.5. However, the uncertainty in effective density differs due to the varying calculation methods used for this quantity. The average effective density is given by

$$\overline{\rho_{\text{eff}}} = \frac{6\overline{m}}{\pi\overline{d_m}^3} = \frac{6s^*\overline{q}}{\pi\overline{d_m}^3}. \quad (4.14)$$

Which has the corresponding uncertainty of

$$\frac{u_{\rho_{\text{eff}}}}{\rho_{\text{eff}}} = \sqrt{\left(\frac{u_{s^*}}{s^*}\right)^2 + \left(\frac{u_{\overline{q}}}{\overline{q}}\right)^2 + 9\left(\frac{u_{d_m}}{d_m}\right)^2}. \quad (4.15)$$

Assuming an 100 fA electrometer signal. This equates to uncertainty in the mean charge of 5.4% and uncertainty in the mobility diameter of 7.3%. The uncertainty in CPMA mass-to-charge set-point is often taken as equal to 2.7% as per [192]. However, the manufacturer now specifies an uncertainty of 5%. The uncertainty is therefore taken as equal to 5%. Combining these gives an uncertainty in the effective density of 22.5%.