Two Dimensional Size-Mass Distribution Function Inversion from Differential Mobility Analyzer- Aerosol Particle Mass Analyzer (DMA-APM) Measurements

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ABSTRACT

We develop and apply a data inversion routine to determine the number based size-mass distribution function (the two dimensional distribution function) from tandem differential mobility analyzer-aerosol particle mass analyzer (DMA-APM) measurements. The two dimensional distribution function is expressed in units of particle number concentration per unit mobility diameter per unit particle mass. It can be used to directly calculate the number based size distribution (commonly determined using DMA measurements) or the mass based size distribution (commonly inferred from impactor measurements). The inversion routine utilizes the Twomey-Markowski algorithm and is applied in this study to DMA-APM measurements of sodium chloride, cesium iodide, and ammonium sulfate particles in the 30-200 nm mobility diameter range, as well as acetylene flame generated soot aggregates in the 40-350 nm range. To utilize the inversion routine, the APM transfer function must be known *a priori*. Here it is computed using a modified version of the Ehara (uniform flow) model, with a transmission correction factor inferred from measurements. For the three examined salt particle types, visual representation of the two dimensional distribution function reveals that at a given mobility diameter, particles have very narrow mass distributions, with the peak masses in good agreement with predictions based on bulk salt densities. However, for soot particles, extremely broad distributions are observed. Soot measurements are compared to predictions for quasifractal aggregates in the transition regime; this comparison suggests that aggregates with fractal dimensions ranging from 1.4-2.5 are all generated in the same system. Finally, we determine the two-dimensional distribution function for a mixture of ammonium sulfate and soot particles, demonstrating that these two particle populations are separable from one another via mobility-mass analysis.

1. INTRODUCTION

Tandem measurement techniques are methods in which analytes are characterized by two orthogonal properties (e.g. size and chemical composition). They are well suited for the characterization of complex mixtures. Aerosols, particularly ambient aerosols, commonly contain a complex mixture of particles of variable size, shape, and chemical composition (McMurry *et al.*, 2000). For this reason, tandem measurement techniques have been and continue to be successfully employed in aerosol analysis (Park *et al.*, 2008). A particularly promising tandem measurement approach to characterize nano- and submicrometer particles is mobility based size analysis with a differential mobility analyzer (DMA (Knutson & Whitby, 1975)) in series with mass analysis with an aerosol particle mass analyzer (APM (Ehara *et al.*, 1996; Tajima *et al.*, 2013)) or centrifugal analyzer (Olfert & Collings, 2005)). This technique (DMA-APM analysis (McMurry *et al.*, 2002; Kuwata, 2015)) yields the mass of mobility selected particles, and hence can yield parameters such as the effective density (Park *et al.*, 2003a; Olfert *et al.*, 2007; Schmid *et al.*, 2007) and dynamic shape factor (Scheckman *et al.*, 2009; Shin *et al.*, 2009; Beranek *et al.*, 2012) of the analyzed particles. DMA-APM analysis and equivalent approaches have been successfully applied in numerous instances (Park, *et al.*, 2003a; Park *et al.*, 2004; Geller *et al.*, 2006; Ku *et al.*, 2006; Kuwata & Kondo, 2009; Scheckman, *et al.*, 2009; Shin *et al.*, 2010; Bladh *et al.*, 2011; Eggersdorfer *et al.*, 2012; Nakao *et al.*, 2013; Grohn *et al.*, 2014; Schnitzler *et al.*, 2014; Boies *et al.*, 2015; Graves *et al.*, 2015; Johnson *et al.*, 2015). However, coupled with appropriate data inversion techniques, DMA-APM analysis could provide an even more complete description of the sizes and morphologies of the particles examined. For example, as suggested by Park *et al.* (2003b), with proper data inversion DMA-APM measurements would yield the shape and material independent mass distribution functions of

particles. In addition, though in most instances a single mass has been linked to particles of a specific mobility equivalent diameter (e.g. in effective density analysis (Gysel *et al.*, 2011; Johnson *et al.*, 2014)), non-spherical particles (in particular combustion derived particles) may not exhibit a singular mass-mobility size relationship. More complete characterization of the structures of morphologically diverse particles will require an appropriate data inversion routine to be coupled to DMA-APM measurements.

Data inversion techniques are required when at least one of the instruments applied in measurement is of modest resolving power or has imperfect transmission. Both conditions are met for DMAs and APMs. In utilizing DMAs alone for size distribution analysis, data inversion techniques are employed ubiquitously (Crump & Seinfeld, 1982; Hagen & Alofs, 1983; Markowski, 1987; Wolfenbarger & Seinfeld, 1990; Collins *et al.*, 2002; Wiedensohler *et al.*, 2012). Data inversion in differential mobility analysis yields the number based size distribution function, $\frac{dn}{dd_p}$ (the number concentration per unit diameter), which, when integrated over the mobility diameter (d_p), yields the particle number concentration, n_{tot} . The purpose of this report is to develop and test a data inversion technique applicable to DMA-APM measurements. Akin to the one-dimensional size distribution function, DMA-APM data inversion yields the two-dimensional number based size-mass distribution function, $\frac{\partial^2 n}{\partial d_p \partial m_p}$ (the number concentration per unit mobility diameter per unit mass). To our knowledge, a multidimensional distribution function has not been inverted from DMA-APM measurements previously. The utility of the two dimensional distribution function is that it can yield both the number based size distribution function and the mass based size distribution function ($\frac{dM}{dd_p}$, the particle mass concentration per unit diameter) through the relationships:

$$\frac{dn}{dd_p} = \int_0^\infty \frac{\partial^2 n}{\partial d_p \partial m_p} dm_p \quad (1a)$$

$$\frac{dM}{dd_p} = \int_0^\infty m_p \frac{\partial^2 n}{\partial d_p \partial m_p} dm_p \quad (1b)$$

Similarly, through integration of the two dimensional distribution function, properties such as the number based mass distribution function ($\frac{dn}{dm_p}$, the number based mass distribution function) as well as the cumulative number and mass concentrations can be directly calculated. In the subsequent sections we describe the experimental system used in testing the inversion routine to determine $\frac{\partial^2 n}{\partial d_p \partial m_p}$ from DMA-APM measurements, the inversion routine itself, and application to measurements of sodium chloride, cesium iodide, ammonium sulfate, and soot particles. The mathematical details of the inversion routine are provided in the supplemental information. Finally, through visualization of the two dimensional size-mass distribution function, we show that morphologically distinct populations of particles can be separated from one another.

2. EXPERIMENTAL & NUMERICAL METHODS

Differential Mobility Analyzer-Aerosol Particle Mass Analyzer Measurements

Though the solution techniques applied in data inversion are general (and can be employed for a variety of instruments (Wolfenbarger & Seinfeld, 1990)) the specific equations applied are dependent on the features of instruments used. As we are concerned with data inversion with DMA-APM measurements, we first describe the tandem measurement system. A schematic diagram is provided in Figure 1. Similar to prior DMA-APM studies (McMurry, et al., 2002; Park, et al., 2003a; Scheckman, et al., 2009; Eggersdorfer, et al., 2012), aerosols were sampled into a single stage impactor (removing most particles larger than 400 nm), followed by a

Po-210 bipolar ion source (labelled as a “neutralizer” in Figure 1) to bring particles to a near steady-state charge distribution (Wiedensohler, 1988; Gopalakrishnan *et al.*, 2013). Following the bipolar charger, particles then entered aDMA (with dimensions identical to model 3081, TSI Inc., Shoreview, MN, USA) at a flowrate of 0.8 l min^{-1} . The DMA was operated with a recirculating sheath flow of air at a rate of 4 l min^{-1} and was calibrated in separate experiments using NIST certified 60 nm polystyrene latex particles. The DMA was operated in stepping mode with a potential difference in the 0 V to 5000 V range. Positively charged particles were classified by the DMA, and those transmitted entered the APM (model 3601, Kanomax Japan Inc., Suita, Osaka, Japan (Tajima, et al., 2013)). The APM was operated with a fixed rotational velocity of 5500-8000 rotations per minute, and for each DMA voltage applied, the voltage on the APM was stepped in the 0 V to 1500 V range. The APM was also calibrated via the measurement of DMA selected 60 nm polystyrene latex particles, with the peak mass in CPC counts found to agreement with the expected mass to within 5%. The flow exiting the APM was then split, with 0.3 l min^{-1} entering a condensation particle counter (CPC, model 3025, TSI Inc.(Stolzenburg & McMurry, 1991)) and the remainder sent to a filter. A LabviewTM program was developed to control the voltages applied to both the DMA and APM, the dwell time for each set of voltages (during which CPC signal was measured), the number of DMA and APM settings applied, and the delay time between measurements. For the reported results we used 35 DMA voltage settings and 50-70 APM settings (1750-2450 individual measurement channels for each sample), with the DMA and APM voltages both varied exponentially (as is commonly performed for DMA based size distribution measurements).

Inversion of the Two Dimensional size-mass distribution function

DMA-APM tandem measurements are directly quantified by CPC measured number concentrations, $N_{i,j}$, which depend upon DMA settings (i) and APM settings (j). These number concentrations are linked to $\frac{\partial^2 n}{\partial d_p \partial m_p}$ through the relationship:

$$N_{i,j} = \sum_{z=+1}^{\infty} \int_0^{\infty} \int_0^{\infty} \Lambda_i(z, d_p) \Theta_j(z, d_p, m_p) \epsilon_{CPC}(d_p) \epsilon_T(d_p) f(z, d_p) \frac{\partial^2 n}{\partial d_p \partial m_p} dd_p dm_p (2)$$

where z is the particle (integer) charge state, $\Lambda_i(z, d_p)$ is the DMA transfer function (the probability a particle of charge state z and mobility diameter d_p is transmitted through the DMA with voltage setting i), $\Theta_j(z, d_p, m_p)$ is the APM transfer function (the probability a particle of charge state z and mass m_p is transmitted through the APM with voltage setting j , which also depends upon the mobility diameter), $\epsilon_{CPC}(d_p)$ is the CPC detection efficiency, $\epsilon_T(d_p)$ is the transport efficiency through system tubing, and $f(z, d_p)$ is the fraction of particles of diameter d_p with charge state z , at the exit of the Po-210 source. For the DMA transfer function, we use the equations provided by Stolzenburg&McMurry(2008). These equations, which account for diffusional broadening and deposition, are provided in the supplemental information. Though several recent studies have been devoted to examination of the transfer functions of aerosol particle mass analyzers (Ehara, et al., 1996; Olfert, 2005; Olfert *et al.*, 2006; Lall *et al.*, 2009; Tajima *et al.*, 2011; Lin *et al.*, 2014), simple-to-apply equations which consider fluid flow profile influences not available. We therefore opt to apply the equations of Ehara et al (1996), who described the transfer function considering uniform flow axially though the device. To also consider inlet and outlet losses within the transfer function, we modify it such that $\Theta_j(z, d_p, m_p)$ is equal to:

$$\Theta_j(z, d_p, m_p) = \frac{\Theta_{j,E}(z, d_p, m_p)}{\zeta} \quad (3)$$

where ζ is a correction factor accounting for transmission losses in the APM and which is determined experimentally, and $\Theta_{j,E}(z, d_p, m_p)$ is the idealized APM transfer function from Ehara et al (also provided in the supplemental information). For ϵ_{CPC} we assume a constant of 0.98 as the CPC utilized is capable of detecting particles down to 2.5 nm in diameter (Stolzenburg & McMurry, 1991). $\epsilon_T(d_p)$ is based on the Gormley-Kennedy equations (Gormley & Kennedy, 1949), and calculated considering the entire length of measurement system tubing (but omitting the DMA). For $f(z, d_p)$ we use the regressions for spheres provided by Gopalakrishnan et al (2013). The Gormley-Kennedy equations and the Gopalakrishnan regression equations are listed in the supplemental information as well. Though it is more common to apply the Wiedensohler (1988) equations to describe $f(z, d_p)$, we opt to use the regression equations of Gopalakrishnan et al (which differ primarily in the expected fractions of doubly charged particles) both because they were developed free of the assumptions of flux matching theory (which lead to an underestimation of the fractions of multiply charged particles (Fuchs, 1963)) and because they are based upon an input ion distribution measurement experimentally in our laboratory (hence the input ion properties examined are likely similar to those of the ions produced in our experiments). We apply these equations to all particles, irrespective of morphology, as in prior numerical and experimental work we have found that when controlling for ion properties, the effect of particle morphology on the bipolar charge distribution is small (Gopalakrishnan, et al., 2013; Gopalakrishnan *et al.*, 2015a).

The goal of data inversion is to determine $\frac{\partial^2 n}{\partial d_p \partial m_p}$ from measurements of $N_{i,j}$ values via equation (2). Here, we infer $\frac{\partial^2 n}{\partial d_p \partial m_p}$ using a Twomey-Markowski algorithm (Twomey, 1975;

Markowski, 1987), which has been adopted in the past in inverting DMA-CPC measurements. This algorithm is described in detail in the supplemental information, where we show how to apply it to DMA measurements (the one dimension case, as is described in prior studies) and subsequently how to apply this algorithm to DMA-APM measurements (the two dimensional case). Briefly, the Twomey-Markowski algorithm involves three steps: (a.) determination of an appropriate initial trial distribution function, (b.) comparison of calculations based upon the trial distribution function to measured $N_{i,j}$ values, (c.) modification of the trial distribution function based upon the comparison in (b.), and (d.) a smoothing step as described by Markowski (1987). These four steps are repeated until a specific error criterion is satisfied, at which time the final trial distribution function is accepted as faithful to the true distribution function.

In addition to listing the transfer functions applied in inversion and providing a description of the inversion routine, the supplemental information contains a parametric study in which a simulated $\frac{\partial^2 n}{\partial d_p \partial m_{p_{sim}}}$ function is input into equation (2) for the calculation of $N_{i,j}$ values (for a selected number of i and j) and the Twomey-Markowski algorithm is used to invert out a function $\frac{\partial^2 n}{\partial d_p \partial m_{p_{inv}}}$. The output distribution function is compared directly to the input to examine the capabilities of the Twomey-Markowski algorithm. In testing the inversion routine, we considered all functions in equation (2), but with $\zeta = 1$ assumed. We show error calculations as functions of both iteration number and the number of measurement channels. The latter number cannot be optimized through inversion; the number of channels is chosen *a priori*. Through example calculations we show that a sufficient number of channels (more than 1500) were used in measurements here. Finally, in the supplemental document we provide a direct

comparison between $\frac{\partial^2 n}{\partial d_p \partial m_{p_{sim}}}$ and inverted $\frac{\partial^2 n}{\partial d_p \partial m_{p_{inv}}}$ for varying numbers of measurements channels, as well as a comparison between equation (1a) and (1b) size and mass distribution functions before and after inversion. Readers interested in the details of the numerical algorithm are thus strongly encouraged to refer to the aforementioned supplemental document; we devote the remainder of the main text to application of the inversion routine to experimental measurements.

Test Aerosols

Four test aerosol samples were examined experimentally in this study; aqueous solutions of sodium chloride (20 mM), cesium iodide (20 mM), and ammonium sulfate (10 mM) were nebulized (in air) in a custom-made nebulizer with the produced droplets dried in a silica-bead diffusion dryer. Nebulization followed by droplet drying produced polydisperse particles in the 20-350 nm mobility diameter range. We also produced soot particles in a diffusion flame, operating with acetylene as the fuel (0.3 l min⁻¹) and oxygen (0.8 l min⁻¹) and nitrogen (~3 l min⁻¹) added as coflow. All gases were of high purity and purchased from Matheson Gas. Soot particles were sampled using a conical sampler and diluted with a flow of N₂. A portion of this flow was sampled into the DMA-APM system. A mixture of nebulizer produced ammonium sulfate and flame produced soot was also examined in DMA-APM measurements. For all measurements, the dwell time at each DMA-APM voltage setting was 7 seconds, the delay time between changes to the APM voltage was 5 seconds, and the delay time between DMA voltages was 20-30 seconds.

3. RESULTS & DISCUSSION

DMA-APM Raw Data

DMA-APM raw data takes the form of $N_{i,j}$ values as functions of both the APM set voltage and DMA set voltage. These voltages can be converted to particle masses and mobility diameters assuming that all particles are singly charged (subsequent inversion corrects for multiply charged particles). In figure 2 we display contour plots of $N_{i,j}$ (expressed as particles per cm^3) as a function of particle mass (expressed in Daltons, **which facilitates estimation of the number of molecules/atoms in each particle**) and mobility diameter (expressed in nanometers) for (a.) sodium chloride, (b.) cesium iodide, (c.) ammonium sulfate, and (d.) soot particles, without correcting for multiply charged particles. Polynomial spline fitting is used in generating these plots, and the measured number concentrations are represented colorimetrically on a logarithmic scale. For the three salt particle types, at a given mobility diameter, particles are only detected in a narrow mass range; this indicates that particles adopt a narrow range of morphologies. However, also at a specific diameter, a secondary peak at higher mass is discernable. This peak corresponds to doubly charged particles, as is commonly observed in contour plots generated in related ion mobility spectrometry-mass spectrometry measurements ((Kanu *et al.*, 2008; Larriba *et al.*, 2011)). **The detected signal at all diameters above 5×10^9 Da in figure 2c was found to be noise during the ammonium sulfate measurement (it is below $20 \text{ particles cm}^{-3}$), though the precise source of this noise signal was never identified.** For the soot particles, at a given mobility diameter, a significantly broader distribution in mass is evident as compared to the noted salt particles. This suggests that (1) soot particles adopt a wider range of morphologies and (2) soot production was likely transient. Though attempts were made to stabilize flame operation, as measurements required several hours of data collection, transient behavior was difficult to avoid. However, we believe this behavior would influence only the

absolute value of CPC measurements and has no bearing on the presence or absence of particles of specific morphologies.

Size Distribution Measurements

Raw data contour plots can be produced without considering instrument and tubing transmission functions. However, prior to inverting measurements to yield $\frac{\partial^2 n}{\partial d_p \partial m_p}$, it is necessary to evaluate (approximately) the APM transfer function, which we assume follows the functional form provided in equation (3). Rigorously, ζ is a function of particle mass, mobility diameter, charge state, as well as the dimensions and operating conditions of the APM. Complete determination of this function would hence provide a complete description of the APM transfer function and its departures from ideal behavior (i.e. the influences of inlet and outlet losses, including diffusional, electrostatic, and inertial mechanisms, would be accounted for). However, at this juncture, we simply wish to provide an estimate of ζ enabling accurate inference of $\frac{\partial^2 n}{\partial d_p \partial m_p}$ under the operating conditions we applied; the procedure we apply could be repeated for any set of test aerosols and APM operating conditions. To estimate ζ , we independently made DMA-CPC measurements for the three salt particle types. As discussed in the introduction and shown in the supplemental information example, DMA-CPC measurements can be inverted to yield $\frac{dn}{dd_p}$. With a correct APM transfer function, calculation of $\frac{dn}{dd_p}$ with equation (1a) should provide a similar result to DMA-CPC inversion. We therefore approximate ζ by fitting, such that equation (1a) calculations of $\frac{dn}{dd_p}$ (performed subsequent to inversion of $\frac{\partial^2 n}{\partial d_p \partial m_p}$ from the data displayed in figure 2) are in good agreement with $\frac{dn}{dd_p}$ inverted solely from

DMA-CPC measurements for all salts. In figure 3, we plot the results of this comparison for (a) sodium chloride, (b) cesium iodide, and (c) ammonium sulfate particles. Soot particles were not used for this comparison because of the observed transient nature of the flame generator, i.e. the size distribution function varied over time, hence the size distribution function measured by the DMA-CPC and DMA-APM-CPC were not necessarily identical. In all plots black circles represent the DMA-CPC inverted $\frac{dn}{dd_p}$ distribution, red triangles represent equation (1a) calculated $\frac{dn}{dd_p}$ values with $\zeta = 1.00$, and open blue squares represent equation (1a) calculated $\frac{dn}{dd_p}$ values with $\zeta = 2.32$. The latter ζ value is simply the average count weighted value considering all salts; considering salt types independently we obtained $\zeta = 2.52, 2.35, 2.10$ for sodium chloride, cesium iodide, and ammonium sulfate, respectively. In determining number based size distribution functions with equation (1a), after performing integration we applied a single Markowski (1987) smoothing step (equations S12a-c in the supplemental information). As evidenced in the figures, reasonably good agreement between DMA-CPC inferred size distribution functions and DMA-APM-CPC inferred size distribution functions is found with $\zeta = 2.32$. Further, integration of $\frac{dn}{dd_p}$ obtained with both methods (over the same bounds) typically yields number concentrations within 10% of one another, except for sodium chloride particles where the differences are larger. Although this suggests that the applied functional form of the APM transfer function (equation 3) for the conditions examined will enable reasonable estimation of $\frac{\partial^2 n}{\partial d_p \partial m_p}$, surprising about this result is that only a constant value of ζ was necessary to bring DMA-CPC and DMA-APM-CPC results in line with one another. One possible explanation is that in the size range examined, the smallest particles are lost in the APM via diffusion or electrostatic deposition in the inlet/outlet, while the largest are subject to inertial

deposition, i.e. though ζ is size dependent it is approximately constant in the 20-350 nm size range because of the disparate size dependencies of these deposition mechanisms. We note that data inversion techniques for DMA-APM measurements would benefit tremendously from clearer determination of the APM (or equivalent mass analyzer) transfer function under a wide variety of conditions, both experimentally and numerically (Olfert, 2005; Olfert, et al., 2006; Lin, et al., 2014). Further, we do not advocate the use of equation (1a) with $\zeta = 2.32$ outside of the particle size range and APM settings applied here; without an improved APM transfer function ζ values will need to be determined on a case-by-case basis.

Inverted Size-Mass Distribution Functions

Contour plots of the inverted number based size-mass distribution functions, $\frac{\partial^2 n}{\partial d_p \partial m_p}$, are shown in figure 4 (a-d), similar to the raw data contour plots in figure 2 (a-d). Distribution functions were determined via equation (2) with the Twomey-Markowski inversion algorithm and $\zeta = 2.32$. All displayed distribution functions are the result of more than 1000 iterations with overall error (Kandlikar & Ramachandran, 1999), as defined the supplemental information, below 0.05. We examine several features of plots. First, we note that the size-mass distribution function is expressed in standard units of number of particles per m^4 per kg, leading to the large values noted on contour plots. Second, for the three salt particle types, the doubly charged peaks apparent in the raw data are substantially diminished in the distribution function contour plots; this is best evidenced through comparison of figure 2c to figure 4c. The reduction of the multiply charged peaks indicates that the assumed charge distribution function (Gopalakrishnan, et al., 2013) approximated the true charge distribution reasonably well; **nonetheless, improvements could be made to more completely removed multiply charged particle peaks from**

the inverted distribution functions. Third, the three salt particle types display a near singular mass-mobility diameter relationship. We can compare this to an effective density model, expressed as:

$$m_p = \frac{\pi}{6} \rho_{eff} d_p^3 \quad (4)$$

where ρ_{eff} is the effective particle density. In each salt particle contour plot we display a solid white line which corresponds to ρ_{eff} equivalent to the bulk salt density (sodium chloride $\rho_{eff} = 2170 \text{ kg m}^{-3}$, cesium iodide $\rho_{eff} = 4150 \text{ kg m}^{-3}$, ammonium sulfate $\rho_{eff} = 1770 \text{ kg m}^{-3}$). Dashed white lines denote effective densities $\pm 10\%$ the bulk density. Good agreement is found between the bulk density curves and peaks in the two dimensional size-mass distribution function. Though such agreement has been obtained before in DMA-APM measurements (Lall, et al., 2009), here it indicates that salt particles adopted relatively compact morphologies and numerical distortion did not occur during data inversion.

For soot particles, broader size-mass distributions functions are obtained than are found for salt particles. Prior measurements show clearly that such particles are not spherical, and typically take the form of chain-like, quasifractal aggregates (Cai *et al.*, 1993). In analyzing DMA-APM measurements of aggregates, the approach commonly adopted is to plot the peak mass (for a given mobility diameter) as a function of mobility diameter; from these plots mass-mobility exponent “x” ($m_p \propto d_p^x$) is inferred. However, as remarked on by Sorensen (2011) and examined in our group (Thajudeen *et al.*, 2012; Zhang *et al.*, 2012; Thajudeen *et al.*, 2015), the mass-mobility exponent is not directly a function of the fractal dimension, which is defined via the scaling between aggregate mass and radius of gyration. In fact, in the transition regime of drag (which applies to nanoparticles and submicrometer particles), wherein the mobility is dependent on an appropriately defined Knudsen number (gas mean free path to particle size

ratio), the mass-mobility exponent depends upon both the particle morphology as well as the Knudsen number. Therefore, while some studies have attempted to develop links between the mass-mobility exponent and aggregate morphology (Eggersdorfer, et al., 2012), such relationships only rigorously apply to aggregates of specific morphologies and under specific measurement conditions (gas composition, temperature, pressure). Further complications in mass-mobility exponent inference manifest themselves instances where the aerosol is transient and the mass distribution at a specific mobility diameter is considerably broad (i.e. when the aggregates are morphologically heterogeneous). Evidenced in figure 4d, these circumstances are encountered here for acetylene flame generated soot aggregates, and would likely be encountered in most combustion systems.

We therefore opt to compare soot aggregate measurements to theoretical predictions for quasifractal aggregates in the transition regime. In the supplemental information, TEM images of several soot aggregates are displayed; these images were used to determine an average primary particle radius of ~12 nm (200 primary particles measured). In the quasifractal aggregate model, the input primary particle radius (a_p), pre-exponential factor (k), and fractal dimension (D_f), are linked to the number of primary particles in an aggregate (N_{prim}) and the aggregate radius of gyration (R_g) through the equation $N_{prim} = k \left(\frac{R_g}{a_p} \right)^{D_f}$. With prescribed N_{prim} , k , a_p , and D_f , the orientationally averaged hydrodynamic radius (R_H) and orientationally averaged projected area (PA) of an aggregate can be calculated. Regression equations to these calculations are provided by Thajudeen et al (2012) for $k = 1.3$ and $D_f = 1.4-2.5$, and are shown in the supplemental information here. Several experimental and theoretical studies (Dahneke, 1973; Cheng *et al.*, 1988; Thajudeen, et al., 2012; Zhang, et al., 2012; Gopalakrishnan *et al.*, 2015b;

Thajudeen, et al., 2015) show that the mobility Z_p of an unaligned aggregate/non-spherical particles can be calculated via the equation:

$$Z_p = \frac{ze}{6\pi\mu R_H} \left(1 + \frac{\lambda\pi R_H}{PA} \left(1.257 + 0.4 \exp \left(-\frac{1.1PA}{\lambda\pi R_H} \right) \right) \right) \quad (5a)$$

where e is the unit electron charge, λ is the hard sphere gas mean free path, and μ is the gas dynamic viscosity. Subsequently, the mobility equivalent diameter (d_p) can be calculated by the equation:

$$Z_p = \frac{ze}{3\pi\mu d_p} \left(1 + \frac{2\lambda}{d_p} \left(1.257 + 0.4 \exp \left(-\frac{0.55d_p}{\lambda} \right) \right) \right) \quad (5b)$$

As the mass of an aggregate can be approximated as $m_p = \frac{4\pi}{3} \rho a_p^3$, where ρ is the bulk density (2267 kg m⁻³ for carbon black), through selection of k and D_f , a specific m_p versus d_p curve can be obtained via equations (5a) & (5b). For $k = 1.3$ and $D_f = 1.4, 1.7, 2.1$, and 2.5 , lines are overlaid on the contour plot of figure 4d. The highest distribution function values are found close to the $D_f = 1.7$ curve, in line with aggregates formed by diffusion limited cluster aggregation predictions (Sorensen, 2011). However, the broadness of the distribution function suggests that aggregates with both higher and lower fractal dimension are present as well. The higher fractal dimension aggregates presumably form via restructuring and sintering. The apparently lower fractal dimension aggregates may actually be those of lower k value than 1.3, as suggested by Heinson et al (Heinson *et al.*, 2010, 2012). However, we elect not to plot lines for $k \neq 1.3$, as it is not our intention to precisely describe all aggregate morphologies. Nonetheless, the presented comparison between quasifractal aggregate model predictions and the size-mass distribution function contour plot shows that quasifractal model prediction are in line with measurements and that a wide range of aggregate morphologies must have been produced during experiments. We suspect the latter conclusion would be found upon application of data inversion to DMA-APM

measurements in most inhomogeneous high temperature synthesis systems. We also argue that use of mass-mobility exponents incompletely describes non-spherical particle morphologies in most systems.

Mass Weighted Size Distributions

A key advantage of $\frac{\partial^2 n}{\partial d_p \partial m_p}$ determination is that a number of one dimensional distribution functions can be calculated from it, not only the number based size distribution function but also a number of others, including the mass based size distribution function ($\frac{dM}{dd_p}$, equation 1b). Mass based sized distributions were first inferred using DMA-APM measurements by Park et al (2003b); however, they did so assuming a singular mass for particles of a given mobility diameter, $m_p(d_p)$, and applying the relationship $\frac{dM}{dd_p} = \frac{dn}{dd_p} m_p(d_p)$. This approach is not applicable to morphologically diverse particles, such as the soot examined here. Noteworthy about the mass based size distribution function is that it cannot be inferred from DMA-CPC measurements or APM-CPC measurements alone. Further, cumulative distribution functions can be computed directly from it, i.e. it can be used to compute particle mass concentration in defined diameter ranges. For all four measured particle types, we plot $\frac{dM}{dd_p}$ in figure 5. As with the number based size distribution functions, we applied a single Markowski (1987) smoothing step $\frac{dM}{dd_p}$ after integration. As compared to the number based distribution functions shown in figure 3, mass based distribution functions are shift towards larger diameters. The non-monotonic behavior of the soot distribution is indicative of the transient behavior of the flame over the course of measurements (several hours).

Mixture Analysis

As a final application of DMA-APM measurement and inversion, we elected to make measurements of externally mixed ammonium sulfate and flame generated soot particles. The raw data, inverted size-mass distribution function, number based size distribution function, and mass based size distribution function are shown in figures 6(a-d), respectively. Again, in generating the results shown in figures 6c & 6d, we applied equations (1a) & (1b), respectively, with Markowski (1987) smoothing. The ammonium sulfate particles and soot particles are almost completely separated from one another in both the raw data and inverted distribution function contour plots. However, neither the number based nor mass based size distribution function alone can be used to identify these two separate particle populations. Through integration of the size-mass distribution function over specific, mobility diameter dependent mass ranges, the ammonium sulfate and soot mass based mass distribution functions could be determined, hence DMA-APM measurements could be used to infer distribution functions for specific particle types isolated in a mixture. This type of analysis may find utility in quantification of particle emissions to the ambient from combustion sources, as highly aggregated particles appear in a different area of space on mobility diameter-mass contour plots than do spherical particles. Further refinement and testing of DMA-APM analysis methods will be necessary to examine whether combustion derived particles can be consistently isolated from spheres in tandem measurements.

4. CONCLUSIONS

We have developed a data inversion scheme which yields the two dimensional, number based size-mass distribution function (the two-dimensional distribution function) from DMA-

APM tandem measurements. The inversion routine relies upon the Twomey-Markowski algorithm. We have also demonstrated that the one dimensional distribution functions, such as those typically obtained from DMA measurements, can be calculated directly from the two dimensional, number based size-mass distribution function. Finally, we compared the two-dimensional distribution function results to effective density models and models for the mobility/drag of quasifractal aggregates. In addition to the noted findings in the *Results & Discussion* section, we draw the following conclusions in this work:

1. To exploit the full potential of tandem measurements in aerosol measurement, it is important to develop data inversion schemes yielding two dimensional distribution functions. For example, in commonly employed tandem differential mobility analyzer measurements (Park *et al.*, 2008), particle hygroscopicity or volatility are quantified. Number based size-hygroscopicity/volatility distribution functions could be developed from such measurements using a similar approach to that employed here.
2. Proper inversion of distribution functions is dependent on *a priori* knowledge of the transmission/transfer function of all measurements employed. Here, an ad-hoc approach was taken to approximate the APM transfer function. A simple-to-implement yet mathematically rigorous transfer function needs to be developed for the APM, considering inlet and outlet losses, which would aid in future application of the presented inversion routine.
3. Visualization of the two-dimensional distribution function aids in identifying externally mixed particles of different density/morphology and non-spherical particles of widely ranging morphology. The latter, which are frequently formed in high temperature systems (combustion), have traditionally been quantified via the mass-mobility exponent,

also determined with DMA-APM measurements. We find the information contained with the mass-mobility exponent to be extremely limited, and suggest that comparison of measurements to more rigorous drag models for non-spherical particles provides more information on the morphology of non-spherical particles.

4. As demonstrated in the supplemental information, of order 10^3 CPC measurements (for variable DMA and APM applied voltages) need to be made to recover the two dimensional size-mass distribution function, if the steps between channels are chosen *a priori*. To make such a large number of measurements for most aerosol systems, hours of sampling are required. Future applications of DMA-APM measurements would benefit from the development of dynamic channel stepping routines, in which the voltage steps between channels are varied based on the measured CPC signal intensity (with small steps for high concentration and larger steps for low concentration). In this way, the sampling time required for tandem measurements could be reduced while the ability to invert the two dimensional distribution function from measurements could be retained.

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6. SUPPLEMENTAL INFORMATION

A description of the instrument transfer functions and charge distribution used in equation (2), a description of the inversion routine used to determine the two-dimensional distribution function, a parametric study applying the inversion routine to simulated data for varying numbers of measurement channels, electron micrographs of soot particles, and the equations used to calculate aggregate hydrodynamic radii and projected areas are all available online.

7. REFERENCES

- Beranek, J., Imre, D., & Zelenyuk, A. (2012). Real-Time Shape-Based Particle Separation and Detailed in Situ Particle Shape Characterization. *Analytical Chemistry*, **84**, 1459-1465.
- Bladh, H., Johnsson, J., Rissler, J., Abdulhamid, H., Olofsson, N.E., Sanati, M., Pagels, J., & Bengtsson, P.E. (2011). Influence of soot particle aggregation on time-resolved laser-induced incandescence signals. *Applied Physics B-Lasers and Optics*, **104**, 331-341.
- Boies, A.M., Stettler, M.E.J., Swanson, J.J., Johnson, T.J., Olfert, J.S., Johnson, M., Eggersdorfer, M.L., Rindlisbacher, T., Wang, J., Thomson, K., Smallwood, G., Sevcenco, Y., Walters, D., Williams, P.I., Corbin, J., Mensah, A.A., Symonds, J., Dastanpour, R., & Rogak, S.N. (2015). Particle Emission Characteristics of a Gas Turbine with a Double Annular Combustor. *Aerosol Science and Technology*, 00-00.
- Cai, J., Lu, N., & Sorensen, C.M. (1993). Comparison of Size and Morphology of Soot Aggregates as Determined by Light-Scattering and Electron-Microscope Analysis. *Langmuir*, **9**, 2861-2867.
- Cheng, Y.S., Allen, M.D., Gallegos, D.P., Yeh, H.C., & Peterson, K. (1988). Drag Force and Slip Correction of Aggregate Aerosols. *Aerosol Sci. Technol.*, **8**, 199-214.
- Collins, D.R., Flagan, R.C., & Seinfeld, J.H. (2002). Improved inversion of scanning DMA data. *Aerosol Science and Technology*, **36**, 1-9.
- Crump, J.G., & Seinfeld, J.H. (1982). A New Algorithm for Inversion of Aerosol Size Distribution Data. *Aerosol Science and Technology*, **1**, 15-34.
- Dahneke, B.E. (1973). Slip Correction Factors for Nonspherical Bodies- III The Form of the General Law. *Journal of Aerosol Science*, **4**, 163-170.
- Eggersdorfer, M.L., Grohn, A.J., Sorensen, C.M., McMurtry, P.H., & Pratsinis, S.E. (2012). Mass-mobility characterization of flame-made ZrO₂ aerosols: Primary particle diameter and extent of aggregation. *Journal of Colloid and Interface Science*, **387**, 12-23.
- Ehara, K., Hagwood, C., & Coakley, K.J. (1996). Novel method to classify aerosol particles according to their mass-to-charge ratio - Aerosol particle mass analyser. *Journal of Aerosol Science*, **27**, 217-234.
- Fuchs, N.A. (1963). On the Stationary Charge Distribution on Aerosol Particles in a Bipolar Ionic Atmosphere. *Geofis. Pura Appl.*, **56**, 185-193.
- Geller, M., Biswas, S., & Sioutas, C. (2006). Determination of particle effective density in urban environments with a differential mobility analyzer and aerosol particle mass analyzer. *Aerosol Science and Technology*, **40**, 709-723.
- Gopalakrishnan, R., McMurtry, P.H., & Hogan, C.J. (2015a). Bipolar Charging of Nanoparticles: A Review of Existing and Development of New Analysis Approaches. *Aerosol Science and Technology*, **In Press**. doi:10.1080/02786826.2015.1109053
- Gopalakrishnan, R., McMurtry, P.H., & Hogan, C.J. (2015b). The Electrical Mobilities and Scalar Friction Factors of Modest to High Aspect Ratio Particles in the Transition Regime. *Journal of Aerosol Science*, **82**, 24-39.

- Gopalakrishnan, R., Meredith, M.R., Larriba-Andaluz, C., & Hogan, C.J. (2013). Brownian Dynamics Determination of the Bipolar Steady State Charge Distribution on Spheres and Non-spheres in the Transition Regime. *Journal of Aerosol Science*, **63**, 126-145.
- Gormley, P.G., & Kennedy, M. (1949). Diffusion from a stream flowing through a cylindrical tube. *Proceedings of the Irish Royal Academy*, **52A**, 163-169.
- Graves, B., Olfert, J., Patychuk, B., Dastanpour, R., & Rogak, S. (2015). Characterization of Particulate Matter Morphology and Volatility from a Compression-Ignition Natural-Gas Direct-Injection Engine. *Aerosol Science and Technology*, **49**, 589-598.
- Grohn, A.J., Eggersdorfer, M.L., Pratsinis, S.E., & Wegner, K. (2014). On-line monitoring of primary and agglomerate particle dynamics. *Journal of Aerosol Science*, **73**, 1-13.
- Gysel, M., Laborde, M., Olfert, J.S., Subramanian, R., & Grohn, A.J. (2011). Effective density of Aquadag and fullerene soot black carbon reference materials used for SP2 calibration. *Atmospheric Measurement Techniques*, **4**, 2851-2858.
- Hagen, D.E., & Alofs, D.J. (1983). Linear Inversion Method to Obtain Aerosol Size Distributions from Measurements with a Differential Mobility Analyzer. *Aerosol Science and Technology*, **2**, 465-475.
- Heinson, W.R., Sorensen, C.M., & Chakrabarti, A. (2010). Does Shape Anisotropy Control the Fractal Dimension in Diffusion-Limited Cluster-Cluster Aggregation? *Aerosol Science and Technology*, **44**, I-IV.
- Heinson, W.R., Sorensen, C.M., & Chakrabarti, A. (2012). A three parameter description of the structure of diffusion limited cluster fractal aggregates. *Journal of Colloid and Interface Science*, **375**, 65-69.
- Johnson, T.J., Olfert, J.S., Cabot, R., Treacy, C., Yurteri, C.U., Dickens, C., McAughey, J., & Symonds, J.P.R. (2014). Steady-state measurement of the effective particle density of cigarette smoke. *Journal of Aerosol Science*, **75**, 9-16.
- Johnson, T.J., Olfert, J.S., Cabot, R., Treacy, C., Yurteri, C.U., Dickens, C., McAughey, J., & Symonds, J.P.R. (2015). Transient measurement of the effective particle density of cigarette smoke. *Journal of Aerosol Science*, **87**, 63-74.
- Kandlikar, M., & Ramachandran, G. (1999). Inverse Methods for Analysing Aerosol Spectrometer Measurements: A Critical Review. *Journal of Aerosol Science*, **30**, 413-437.
- Kanu, A.B., Dwivedi, P., Tam, M., Matz, L., & Hill, H.H. (2008). Ion mobility-mass spectrometry. *Journal of Mass Spectrometry*, **43**, 1-22.
- Knutson, E.O., & Whitby, K.T. (1975). Aerosol Classification By Electric Mobility: Apparatus, Theory, and Applications. *Journal of Aerosol Science*, **6**, 443-451.
- Ku, B.K., Emery, M.S., Maynard, A.D., Stolzenburg, M.R., & McMurry, P.H. (2006). In situ structure characterization of airborne carbon nanofibres by a tandem mobility-mass analysis. *Nanotechnology*, **17**, 3613-3621.
- Kuwata, M. (2015). Particle Classification by the Tandem Differential Mobility Analyzer-Particle Mass Analyzer System. *Aerosol Science and Technology*, **49**, 508-520.
- Kuwata, M., & Kondo, Y. (2009). Measurements of particle masses of inorganic salt particles for calibration of cloud condensation nuclei counters. *Atmospheric Chemistry and Physics*, **9**, 5921-5932.
- Lall, A.A., Ma, X.F., Guha, S., Mulholland, G.W., & Zachariah, M.R. (2009). Online Nanoparticle Mass Measurement by Combined Aerosol Particle Mass Analyzer and

- Differential Mobility Analyzer: Comparison of Theory and Measurements. *Aerosol Science and Technology*, **42**, 1075-1083.
- Larriba, C., Hogan, C.J., Attoui, M., Borrajo, R., Fernandez-Garcia, J., & Fernandez de la Mora, J. (2011). The Mobility-Volume Relationship below 3.0 nm examined by Tandem Mobility-Mass Measurement. *Aerosol Science and Technology*, **45**, 453-467.
- Lin, G.Y., Liao, B.X., Tzeng, N.J., Chen, C.W., Uang, S.N., Chen, S.C., Pui, D.Y.H., & Tsai, C.J. (2014). The Effect of Nanoparticle Convection-Diffusion Loss on the Transfer Function of an Aerosol Particle Mass Analyzer. *Aerosol Science and Technology*, **48**, 583-592.
- Markowski, G.R. (1987). Improving Twomey's Algorithm for Inversion of Aerosol Measurement Data. *Aerosol Science and Technology*, **7**, 127-141.
- McMurry, P.H., Dick, W.D., & Wang, X. (2000). Novel measurements of atmospheric aerosol properties. In *Nucleation and Atmospheric Aerosols* (Edited Hale, B.N. & Kulmala, M.), *Nucleation and Atmospheric Aerosols* (Vol. 534, pp. 699-710), City.
- McMurry, P.H., Wang, X., Park, K., & Ehara, K. (2002). The relationship between mass and mobility for atmospheric particles: A new technique for measuring particle density. *Aerosol Science and Technology*, **36**, 227-238.
- Nakao, S., Tang, P., Tang, X.C., Clark, C.H., Qi, L., Seo, E., Asa-Awuku, A., & Cocker, D. (2013). Density and elemental ratios of secondary organic aerosol: Application of a density prediction method. *Atmospheric Environment*, **68**, 273-277.
- Olfert, J.S. (2005). A numerical calculation of the transfer function of the fluted centrifugal particle mass analyzer. *Aerosol Science and Technology*, **39**, 1002-1009.
- Olfert, J.S., & Collings, N. (2005). New method for particle mass classification - the Couette centrifugal particle mass analyzer. *Journal of Aerosol Science*, **36**, 1338-1352.
- Olfert, J.S., Reavell, K.S.J., Rushton, M.G., & Collings, N. (2006). The experimental transfer function of the Couette centrifugal particle mass analyzer. *Journal of Aerosol Science*, **37**, 1840-1852.
- Olfert, J.S., Symonds, J.P.R., & Collings, N. (2007). The effective density and fractal dimension of particles emitted from a light-duty diesel vehicle with a diesel oxidation catalyst. *Journal of Aerosol Science*, **38**, 69-82.
- Park, K., Cao, F., Kittelson, D.B., & McMurry, P.H. (2003a). Relationship between particle mass and mobility for diesel exhaust particles. *Environmental Science & Technology*, **37**, 577-583.
- Park, K., Dutcher, D., Emery, M., Pagels, J., Sakurai, H., Scheckman, J., Qian, S., Stolzenburg, M.R., Wang, X., Yang, J., & McMurry, P.H. (2008). Tandem measurements of aerosol properties - A review of mobility techniques with extensions. *Aerosol Science and Technology*, **42**, 801-816.
- Park, K., Kittelson, D.B., & McMurry, P.H. (2003b). A closure study of aerosol mass concentration measurements: comparison of values obtained with filters and by direct measurements of mass distributions. *Atmospheric Environment*, **37**, 1223-1230.
- Park, K., Kittelson, D.B., & McMurry, P.H. (2004). Structural properties of diesel exhaust particles measured by transmission electron microscopy (TEM): Relationships to particle mass and mobility. *Aerosol Science and Technology*, **38**, 881-889.
- Scheckman, J.H., McMurry, P.H., & Pratsinis, S.E. (2009). Rapid Characterization of Agglomerate Aerosols by In Situ Mass-Mobility Measurements. *Langmuir*, **25**, 8248-8254.

- Schmid, O., Karg, E., Hagen, D.E., Whitefield, P.D., & Ferron, G.A. (2007). On the effective density of non-spherical particles as derived from combined measurements of aerodynamic and mobility equivalent size. *Journal of Aerosol Science*, **38**, 431-443.
- Schnitzler, E.G., Dutt, A., Charbonneau, A.M., Olfert, J.S., & Jager, W. (2014). Soot Aggregate Restructuring Due to Coatings of Secondary Organic Aerosol Derived from Aromatic Precursors. *Environmental Science & Technology*, **48**, 14309-14316.
- Shin, W.G., Mulholland, G.W., Kim, S.C., Wang, J., Emery, M.S., & Pui, D.Y.H. (2009). Friction coefficient and mass of silver agglomerates in the transition regime. *Journal of Aerosol Science*, **40**, 573-587.
- Shin, W.G., Mulholland, G.W., & Pui, D.Y.H. (2010). Determination of volume, scaling exponents, and particle alignment of nanoparticle agglomerates using tandem differential mobility analyzers. *Journal of Aerosol Science*, **41**, 665-681.
- Sorensen, C.M. (2011). The Mobility of Fractal Aggregates: A Review. *Aerosol Science and Technology*, **45**, 765-779.
- Stolzenburg, M.R., & McMurry, P.H. (1991). An Ultrafine Aerosol Condensation Nucleus Counter. *Aerosol Science and Technology*, **14**, 48-65.
- Stolzenburg, M.R., & McMurry, P.H. (2008). Equations governing single and tandem DMA configurations and a new lognormal approximation to the transfer function. *Aerosol Science and Technology*, **42**, 421-432.
- Tajima, N., Fukushima, N., Ehara, K., & Sakurai, H. (2011). Mass Range and Optimized Operation of the Aerosol Particle Mass Analyzer. *Aerosol Science and Technology*, **45**, 196-214.
- Tajima, N., Sakurai, H., Fukushima, N., & Ehara, K. (2013). Design Considerations and Performance Evaluation of a Compact Aerosol Particle Mass Analyzer. *Aerosol Science and Technology*, **47**, 1152-1162.
- Thajudeen, T., Gopalakrishnan, R., & Hogan, C.J. (2012). The Collision Rate of Nonspherical Particles and Aggregates for all Diffusive Knudsen Numbers. *Aerosol Science and Technology*, **46**, 1174-1186.
- Thajudeen, T., Jeon, S., & Hogan, C.J. (2015). The mobilities of flame synthesized aggregates/agglomerates in the transition regime. *Journal of Aerosol Science*, **80**, 45-57.
- Twomey, S. (1975). Comparison of Constrained Linear Inversion and an Iterative Nonlinear Algorithm Applied to Indirect Estimation of Particle-Size Distributions. *J. Comput. Phys.*, **18**, 188-200.
- Wiedensohler, A. (1988). An Approximation of the Bipolar Charge-Distribution for Particles in the Sub-Micron Size Range. *Journal of Aerosol Science*, **19**, 387-389.
- Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjaraa, A.M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J.A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Grunig, C., Faloon, K., Beddows, D., Harrison, R.M., Monahan, C., Jennings, S.G., O'Dowd, C.D., Marinoni, A., Horn, H.G., Keck, L., Jiang, J., Scheckman, J., McMurry, P.H., Deng, Z., Zhao, C.S., Moerman, M., Henzing, B., de Leeuw, G., Loschau, G., & Bastian, S. (2012). Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions. *Atmospheric Measurement Techniques*, **5**, 657-685.

- Wolfenbarger, J.K., & Seinfeld, J.H. (1990). Inversion of Aerosol Size Distribution Data. *Journal of Aerosol Science*, **21**, 227-247.
- Zhang, C.L., Thajudeen, T., Larriba, C., Schwartzentruber, T.E., & Hogan, C.J. (2012). Determination of the Scalar Friction Factor for Nonspherical Particles and Aggregates Across the Entire Knudsen Number Range by Direct Simulation Monte Carlo (DSMC). *Aerosol Science and Technology*, **46**, 1065-1078.

Figure 1. A schematic diagram of the differential mobility analyzer (DMA)- aerosol particle mass analyzer (APM) system used in the reported measurements. CPC: condensation particle counter.

Figure 2. Raw data contour plots of the CPC measured number concentrations (in terms of particles per cm^3) as functions of singly charged equivalent mobility diameter and singly charged equivalent mass, for **(a)** sodium chloride, **(b)** cesium iodide, **(c)** ammonium sulfate, and **(d)** soot particles.

Figure 3. Number based particle size distribution functions $\frac{dn}{dd_p}$, expressed in terms of particle number per m^4 , inverted from measurements for **(a)** sodium chloride, **(b)** cesium iodide, **(c)** ammonium sulfate particles. Black circles: DMA-CPC inverted size distribution functions; Red triangles: DMA-APM-CPC inverted size distribution functions with $\zeta = 1.00$ assumed in equation (3); Open blue squares: DMA-APM-CPC inverted size distribution functions with $\zeta = 2.32$, applied.

Figure 4. Contour plots of the inverted number based size-mass distributions functions, in units of number per m^4 per kg, for (a) sodium chloride, (b) cesium iodide, (c) ammonium sulfate, and (d) soot particles. In plots (a-c), solid white lines corresponding to equation (4) predictions with the effective density equivalent to the bulk salt density, and the dashed white lines represent $\pm 10\%$.

Figure 5. Mass based size distribution functions, determined using equation (1b) with the two dimensional distribution functions displayed in figure 4.

Figure 6. The raw data contour plot (a), number based size-mass distribution function contour plot (b), the number based size distribution function (c), and the mass based size distribution function (d) for a mixture of ammonium sulfate and soot particles.