Densities of internally mixed organic-inorganic particles from mobility diameter measurements of aerodynamically classified aerosols

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ABSTRACT

Accurate knowledge of particle density is essential for many aspects of aerosol science. Yet, density is often characterized poorly and incompletely for internally mixed particles, particularly for dry particles, with previous studies focused primarily on deliquescent (aqueous) droplets. Instead, densities for dry internally mixed particles are often inferred from mass composition measurements in combination with predictive models assuming ideal mixing, with the accuracy of such models not estimated. We determined particle densities from mobility diameter measurements (using a Scanning Mobility Particle Sizer, SMPS) for dried particles classified by their aerodynamic size (using an Aerosol Aerodynamic Classifier, AAC) for a range of two-component organic-inorganic particles containing known proportions of organic and inorganic species. We examined all permutations of mixing between four different organic (water soluble nigrosin dye, citric acid, polyethylene glycol-400, and ascorbic acid) and three different inorganic (sodium chloride, ammonium sulfate, and sodium nitrate) species. The accuracy and precision in our measured particle densities were ~5% and ~1%, respectively, for nonvolatile particles. Substantial deviations in particle density from ideal mixing (up to 20%) were observed. We tested descriptions of the non-ideal mixing for our systems by representing the volume change of mixing using Redlich-Kister (RK) polynomials in terms of mass fraction or in terms of mole fraction, with both approaches performing similarly.

GRAPHICAL ABSTRACT

1. Introduction

Particle density is a critical property for many aspects of aerosol science. It impacts particle aerodynamic properties and is thereby important in understanding the dynamics and lifetimes of particles in air streams. These aerodynamic considerations are key to understanding the behaviors of respirable aerosols and therefore are central to the development of aerosolized pharmaceuticals for drug delivery to the lungs (Edwards et al. 1997, 1998), as well as for modeling the contribution of expiratory droplets to airborne transmission and inhalation of pathogens (Walker et al. 2021). Moreover, understanding and modeling the optical properties of particles and how they interact with sunlight requires us to consider particle density. At a fundamental level, the density influences the...
intensive optical properties (refractive index) of a particle as specified through the Lorentz-Lorenz relation (Liu and Daum 2008). In atmospheric models of aerosol radiative transfer, density descriptions for particles of different aerosol types are needed to calculate mass extinction and absorption coefficients which, in combination with inventories of mass emission rates for different species, allow calculation of the optical depth for aerosol layers (Edwards and Slingo 1996). The densities of many common types of particles remain poorly constrained and represented, even for those with relatively simple chemical compositions, such as pure black carbon (soot) particulates (Olffert and Rogak 2019). Adding further complication to this problem, aerosol particles are commonly internally mixed and can be highly heterogeneous in chemical composition, structure, and phase (Riemer et al. 2019).

Studies have focused on the measurement of density for macroscale (bulk) samples using techniques such as X-ray crystallography (Robie et al. 1967; Johnston and Hutchison 1942) and helium densitometry (Pusz et al. 2010) for solids, the oscillating U-tube method for liquids and gases (Sequeira et al. 2019; Ashcroft et al., 1990), and a magnetic suspension balance (Kuramoto et al. 2004; Wagner and Kleinrahm 2004) for liquids. These techniques provide high precision measurements for single-component bulk samples as well as for mixtures. We refer to these measured densities as material densities. However, the effective density \( \rho_e \) of a particle can be very different from that of the material density of the substance comprising the particle. Leaving a strict definition of \( \rho_e \) to Sect. 2, these differences can arise from the non-spherical and/or aggregate structures that often occur during particle formation, with these morphological effects distributing the particle mass over a larger volume compared to a bulk material (Olffert and Rogak 2019; Pagels et al. 2009; Zelenyuk et al., 2006). Besides morphological impacts on effective density, particles often have compositions that are completely inaccessible to bulk samples. For example, aqueous droplets are able to exist in metastable supersaturated concentration states with respect to the solute, with solute molalities that can exceed the bulk solubility limit by up to several orders of magnitude (Bzdek et al. 2020; Cai et al. 2016). Therefore, it is of key importance to be able to characterize particle densities in addition to material densities. Progress in this area requires new approaches and techniques that enable determinations of densities for different particle compositions and mixing states.

Predicting the densities of chemically complex, internally mixed particles relies on the application of suitable mixing rules. It is common for densities to be calculated using aerosol composition measurements in combination with mixing rules, but these rules often have no physical basis and are chosen for their simplicity. Additionally, there is typically little or no discussion of their accuracy. Most often, studies assume ideal mixing of mixture components. For example, Taylor et al. (2020) use aerosol mass spectrometry data in combination with a volume-fraction weighting of assumed densities for inorganic and organic components of biomass burning aerosol coatings. McMurry et al. (2002) used an ideal mixing rule to calculate the densities of ambient aerosols, assuming that the particles were internally mixed and with fractional contributions from individual inorganic components. These ideal mixing approaches ignore the non-ideal interactions that can occur between individual mixture components that contribute a volume change of mixing. For example, recent work has indicated that crystalline structures of inorganic salts are not able to form upon mixing with organic species in some situations, with large changes in the mixture density occurring for some mixing compositions (Cotterell et al. 2020; Radney and Zangmeister, 2018). The lack of information on how effective density depends on chemical composition, and therefore the lack of assessment of the accuracy of density mixing models, exists because techniques and measurement approaches to directly measure the effective density of particles have only recently become available. With the advent of new and sensitive approaches for effective density measurements for aerosol particles, it is timely for studies to be conducted of effective density dependencies on chemical composition that enable assessments of predictive mixing models. This is of particular importance to atmospheric aerosols, in which a single particle may contain many chemical components of both organic and inorganic species (Murphy et al. 2006).

Particle densities determined from combined measurements of the particle mass, mobility, and/or aerodynamic size distributions have been reported in recent years, and we refer the reader to the article by Peng et al. (2021) who summarize and compare these approaches. In particular, size-resolved density characterizations are achieved with high precision when two of these particle size metrics are measured in tandem such that the distribution in one metric is recorded for particles classified by another metric (Peng et al. 2021). For example, it has become widely adopted to
record the particle mass distribution (using an instrument such as the Centrifugal Particle Mass Analyzer) for particles that are first classified by their mobility, or vice versa from measurements of the mobility diameter distribution (using a Scanning Mobility Particle Sizer; SMPS) for particles first classified by their mass (Hu et al. 2021; Radney and Zangmeister 2018; Eggersdorfer et al. 2012; McMurry et al. 2002). Either of these approaches can be applied to the characterization of effective density for ambient aerosol particles, or for those generated in the laboratory, but they require particles to be charged using a neutralizer immediately prior to the initial classification stage. The subsequent classification of the charged particles by either a mass or mobility analyzer suffers from a poor transmission efficiency because of the small fraction of charged particles following neutralization, with a majority of particles possessing no charge, thus degrading the sensitivity of downstream characterizations of particle size metrics. A very recent innovation is the development of the Aerosol Aerodynamic Classifier (AAC), which classifies particles by their aerodynamic size (or, more strictly, their relaxation time) (Tavakoli et al. 2014; Tavakoli and Olfert, 2013).

As an AAC does not require particles to undergo any prior charging, it yields much higher transmission efficiencies (up to ~5 times higher than the other aforementioned analyzers) while also removing the multiple charging artifacts that can confound retrievals of aerosol microphysical properties (Johnson et al. 2018; Tavakoli et al. 2014; Tavakoli and Olfert, 2013). In this work, an AAC was used to select particles within a narrow range of aerodynamic diameter, and the mobility diameter of these classified particles was measured using an SMPS. The relationship between aerodynamic and mobility size was then used to determine the effective density of the particles.

Only a limited number of studies have examined effective densities of mixed particles. Studies on particles levitated in an electrodynamic balance have allowed the determination of densities for aqueous droplets containing dissolved inorganic or organic solutes (Lienhard et al. 2012; Tang et al. 1997); however, these methods are unable to determine the densities of dry particles that do not resemble perfect spheres, precluding determinations of particle densities at low relative humidity (RH). Indeed, in situ observations of atmospheric particle properties (e.g., optical properties) are largely made on particles that have been dried below their efflorescence RH (e.g., Haywood et al. 2021; Redemann et al. 2021; Wu et al. 2021; Taylor et al. 2020; Davies et al. 2019; Pistone et al. 2019). Zelenyuk et al. (2006) used Single Particle Laser Ablation Time-of-flight mass spectrometry to sample mobility-selected particles, enabling direct measurements of particle densities for dry organic-inorganic particles for two different mixing ratios of succinic or lauric acid with ammonium sulfate. These measurements did not allow for any assessment of density mixing models for the limited range of mixture compositions considered. To our knowledge, no study has yet determined the densities under dry conditions of internally mixed organic-inorganic particles of atmospheric relevance over a comprehensive range of mixture compositions to enable assessments of density mixing models.

In this work, we use the AAC-SMPS approach to investigate particle densities for two-component organic-inorganic particles containing known proportions of an organic and an inorganic species, examining all permutations of mixing between four different organic (water soluble nigrosin dye, citric acid, polyethylene glycol-400, and ascorbic acid) and three different inorganic (sodium chloride, ammonium sulfate, and sodium nitrate) species. The systems of interest are chosen because of their relevance to atmospheric aerosols or aerosol science more broadly. We develop and test density mixing models for our solid mixtures and assess the discrepancies that arise in these predictions when using simplistic ideal mixing rules. The following section explicitly defines effective density and describes the theoretical basis underpinning its determination using the AAC-SMPS approach. We then describe our experimental methods and chemical systems of interest (Sect. 3). Next, we build on studies by other authors to assess the performance of the AAC-SMPS measurement approach in terms of its accuracy, sensitivity, and reproducibility (Sect. 4.1). We then report effective density measurements for different organic-inorganic mixtures and develop and evaluate non-ideal mixing models to describe our measured densities (Sect. 4.2).

**2. Density retrievals from mobility diameter measurements for aerodynamically classified particles**

The effective density of a particle is defined as the ratio of the particle mass \((m)\) to the volume of a sphere with a diameter equal to the particle mobility diameter \((d_m)\) (Tavakoli & Olfert 2014):

\[
\rho_e = \frac{m}{\frac{\pi}{6}d_m^3}
\]  

For spherical particles, \(d_m\) is equivalent to the particle geometric diameter. The effective density can be
determined from measurements of $d_m$ (using an SMPS) for particles first classified on their relaxation time $\tau$ (i.e., their characteristic time of approach to constant velocity when subjected to both centrifugal and drag forces) using an AAC (Tavakoli and Olfert 2013). The AAC consists of two cylinders rotating in the same direction at the same speed that exert centrifugal forces on particles in the radial direction as they are passed through the gap between the cylinders, while a sheath flow transports the particles in the axial direction. By controlling the rotational frequency of the cylinders and the sheath flow rate, only particles within a very narrow range of selected relaxation times are transmitted. This relaxation time is equal to the product of the particle mass ($m = \rho_c \frac{4}{3} \pi d_m^3$) and mobility ($B = \frac{\rho_c (d_m/mae)^2}{18 \mu}$) (Tavakoli and Olfert 2014; Tavakoli et al. 2014; McMurry et al. 2002):

$$\tau = mB = \frac{\rho_c d_m^2 C_e(d_m)}{18 \mu}$$  \hspace{1cm} (2)$$

with $\mu$ the dynamic viscosity of air and $C_e$ the Cunningham slip correction factor (Allen and Raabe 1982). This relaxation time can be expressed in terms of its aerodynamic diameter ($d_{ae}$), which is defined as the diameter of a spherical particle with density $\rho_c = \rho_0 = 1 \text{ g cm}^{-3}$ that has the same relaxation time and given implicitly by the equation (Tavakoli and Olfert 2014; Tavakoli et al. 2014):

$$\tau = \frac{\rho_0 d_{ae}^2 C_e(d_{ae})}{18 \mu}$$  \hspace{1cm} (3)$$

Combining Equations (2) and (3) yields an expression for the effective density in terms of the particle aerodynamic and mobility diameters:

$$\rho_c = \frac{\rho_0 d_{ae}^2 C_e(d_{ae})}{d_m^2 C_e(d_m)}$$  \hspace{1cm} (4)$$

The AAC can be used to classify aerosol particles with a desired $d_{ae}$ from a polydisperse ensemble, while a downstream SMPS measures their mobility diameter distribution. The value of $d_m$ corresponding to the AAC-selected $d_{ae}$ is determined and the effective density is calculated using Equation (4) under the assumption that the particles are spherical. For spherical particles without voids, this calculated density is equal to the density of the bulk material constituting the particle (i.e., $\rho_c = \rho_{\text{bulk}}$). For spherical aerosol particles with voids, the effective density is less than the material density (Tavakoli and Olfert 2014; DeCarlo et al. 2004; Brockmann and Rader 1990), and for particles that are non-spherical (either with or without voids), the effective density derived by the above approach may differ from the material density by an amount that depends on the particle size and shape (Tavakoli and Olfert 2014; McMurry et al. 2002; Hinds 1999). It is common to use the dynamic shape factor ($\chi$) to quantify the impact of particle shape on the discrepancy between the measured effective density and the density of the material constituting the particle ($\rho_m$), with higher $\chi$ values reducing the measured effective density to below that for the material density (DeCarlo et al. 2004). The dynamic shape factor is equal to unity for spherical particles, but is almost always greater than one for non-spherical particles (DeCarlo et al. 2004).

An approach that can be used to examine the dependence of the effective density on the mobility diameter is to express the particle mass as a power law relation in terms of $d_m$:

$$m = A d_m^f$$  \hspace{1cm} (5)$$

with $A$ a constant and $f$ denoted as the mass-mobility exponent. The quantity $f$ is equal to 3 for particles that do not consist of agglomerate chains, while it is in the range 1.96-2.18 for ZrO$_2$ particles (Eggersdorfer et al. 2012), 2.48 for soot particles from non-premixed flames (Olfert and Rogak 2019), 2-3 for soot particles from premixed flames (Cross et al. 2010), and 2.26 ± 0.05 for black carbon particles produced during the flaming combustion of sub-Saharan African biomass fuels (Pokhrel et al. 2021). Combination of Equations (1) and (5) yields:

$$\rho_c = \frac{6A}{\pi} d_m^{-3}$$  \hspace{1cm} (6)$$

This equation captures the size-dependence of effective density. The value $f = 3$ indicates that the density is size-independent. Substitution of Equation (6) for $\rho_p$ into Equation (4) yields the expression:

$$\frac{6A}{\pi} d_m^{-1} C_e(d_m) = \rho_0 d_{ae}^2 C_e(d_{ae})$$  \hspace{1cm} (7)$$

Therefore, from measurements of $d_m$ for different values of AAC-selected $d_{ae}$, the parameters $A$ and $f$ that yield the best fit can be determined, thereby enabling the size-dependent density to be determined using Equation (6). However, it is highly unlikely that the retrieved $f$ will take the exact value $f = 3$ even when sampled particles are perfect spheres because of measurement uncertainties in $d_m$ and $d_{ae}$. Even small (e.g., 1%) differences in $f$ from the value 3 would imply a size-dependent density, thus making it challenging to define the effective density, as a density at a reference diameter would need to be chosen. Therefore, in this work, effective densities are calculated according to Equation (4), and data are analyzed simultaneously.
using the approach summarized by Equation (7) only as a ‘quality control’ method to ensure that the sampled particles have a retrieved \( f \) within an arbitrarily chosen threshold of ±5% of \( f = 3 \), and therefore that they can be considered to have size-independent effective densities.

### 3. Experimental methods

Our approach to measuring effective density is summarized in Figure 1. Briefly, we generated hydrated particles by nebulizing an aqueous solution with a controlled solute composition. The flow rate through the nebulizer (TSI Portable Test Aerosol Generator, Model 3073) was maintained at \( \sim 1 \text{ L min}^{-1} \) by adjusting the pressure of the gas flow at the nozzle inlet of the nebulizer. The sample then passed into a \( \sim 5 \) L glass vessel that served as a buffer to prevent under- or over-pressuring of the downstream measurement instruments. One outlet of this glass vessel was connected to a HEPA filter to facilitate this buffering, and a second outlet allowed the sample to be drawn through our measurement instrumentation. The RH of the sample was reduced to less than 10% (as recorded by the downstream SMPS, see below, which used an RH probe to characterize the humidity of the sheath flow) by drawing the sample through an aerosol diffusion dryer (Cambustion Ltd., Aerosol Diffusion Dryer) filled with indicating silica gel desiccant. The aerosol sample was then classified using an AAC (Cambustion Ltd.).

The sample transmitted by the AAC had a narrow distribution of aerodynamic diameters with a set-point value that was specified by the user. The resolution \( R_s \) of this transmitted distribution, defined as the ratio of the aerodynamic diameter set point to the full width at half maximum, was set to 20. Values of \( d_{ae} \) from 100 to 400 nm in 50 nm intervals were selected, with an additional value of 125 nm chosen for consistency with our early measurements. This \( d_{ae} \) range was chosen to allow subsequent accurate characterizations of particle mobility spectra using an SMPS, which were limited to an upper mobility diameter of <800 nm. For each value of \( d_{ae} \), the mobility size distribution of the AAC-transmitted aerosol sample was characterized using an SMPS, which consisted of a TSI 3082 classifier utilizing a TSI 3088 Advanced Neutralizer, a TSI 3081 Differential Mobility Analyzer (DMA), and a TSI 3756 Condensation Particle Counter (CPC). The CPC operated at a flow rate of 0.3 L min\(^{-1}\), which governed the flow rate through the diffusion dryer, AAC, and mobility classifier. The neutralizer imparted a bipolar charge distribution on the particles in the sample, and the particles were then selected by their mobility through an applied negative voltage to the center electrode of the DMA. This voltage was continuously scanned while the CPC recorded the number concentration of the mobility-classified particles. The sheath flow through the DMA column was set to 3 L min\(^{-1}\) during these mobility distribution measurements, with a total scan time of 300 s over the mobility diameter range 50-600 nm. An inversion algorithm built into the manufacturer’s software (AIM, version 11.0) converted the raw measured size-dependent particle concentrations to a mobility diameter spectrum, with the standard corrections applied for multiple charging artifacts and diffusion losses. The delay time \( t_d \) was calculated automatically by the AIM software based on the length of tubing between the DMA and CPC (measured as 20 cm), and took a value of \( t_d = 1.72 \text{ s} \). All measurements were performed at ambient temperature and neither the temperature of the apparatus nor the laboratory were regulated. The sample temperatures recorded by the SMPS during our measurement period were in the range \( \sim 298 – 305 \text{ K} \). It was expected that the dependence of the measured densities on temperature would be very weak, as it is for most solids away from a phase transition.

The density retrieval approaches described in Sect. 2 require metrics for \( d_m \) corresponding to the nominal \( d_{ae} \). We compared two different metrics for \( d_m \) (see Sect. 4.1). First, we used the modal mobility diameter corresponding to the largest amplitude in the recorded number size distribution (\( dN/d\log(d_m) \)), which we refer to as the mode-average \( d_m \). Second, recognizing

![Figure 1. Schematic diagram summarizing our experimental approach to measurements of aerosol density. HEPA filter is a High Efficiency Particle Air filter, AAC is an Aerodynamic Aerosol Classifier, DMA is a Differential Mobility Analyzer, CPC is a Condensation Particle Counter, and SMPS is a Scanning Mobility Particle Sizer.](image_url)
that the recorded mobility spectra had noise levels that could degrade the accuracy of the mode-average $d_m$ and that the precision in this value is limited by the discrete number of measurement bins in an SMPS scan, we also used the derived modal diameter from the best fit of a bimodal lognormal distribution to the mobility diameter spectrum, which we refer to as $d_{m-fit}$.

Particles produced from solutions of two-component mixtures containing known mass fractions of an organic and an inorganic salt were studied. The mixture composition was controlled by dissolving known mass fractions of the chosen water-soluble organic ($w_{org}$) species and inorganic salt ($w_{inorg}$) in HPLC grade water, with a total solute mass of 1 g added to 80 ml of water. We were required to control the mass fractions, rather than mole fractions, of our solutes because the molecular weights for some of our solutes (specifically, nigrosin) were not known thereby precluding a mole fraction calculation. This aqueous solution was nebulized to generate our test particles using the procedure described above. It was assumed that the composition (i.e., organic-inorganic mass ratios) of the particles were the same as that of the solution. We note that the solubility limits of our chosen chemical species were all greater than $\sim 350 \text{ g L}^{-1}$ and therefore our aqueous solution concentrations (12.5 g L$^{-1}$) were well below these limits, removing any impact of solute solubility in our aqueous nebulizer solutions on the composition of our generated particles. Nominaly, mixture compositions were varied systematically over the $w_{org}$ range of 0.0 – 1.0 in 0.1 intervals. As measurements progressed, some additional compositions at intermediate $w_{org}$ values were occasionally studied when the calculated density was found to be particularly sensitive to mixture composition. Repeat measurements were also performed for selected organic-inorganic mixtures at specific compositions. These repeats were mostly made in the early stages of our experimental studies when we were interested in the reproducibility of our derived densities. The value of $\rho_e$ of a given organic-inorganic mixture composition was calculated using Equation (4) from AAC-selected $d_{ae}$ values and the measured mode-average $d_m$ or fitted $d_{m-fit}$ values. In addition, values of $f$ and $A$ were determined using Equation (7) by minimizing the weighted least-squares residuals between $[6A/\pi] d_m^{d_m-1} C_e(d_m)$ and $\rho_e d_{ae}^{d_{ae}-1} C_e(d_{ae})$, with the retrieved $f$ used only to check that the densities of the sampled particles could be considered as size-independent.

We determined the effective densities of two-component mixtures for all the permutations of mixing for four organic species with each of three inorganic salts. The inorganic salts used, ammonium sulfate (AS), sodium nitrate (SN), and sodium chloride (SC), were chosen because of their importance to atmospheric aerosol composition (Cotterell et al. 2017; Tang et al. 1997; Tang and Munkelwitz 1994). The organic species, water-soluble nigrosin dye (Nig, CAS code: 8005-03-6, batch number: BCBG2998V), citric acid (CA), polyethylene glycol 400 (PEG), and L-ascorbic acid (AA), were chosen based mostly on their importance to aerosol science, with Nig used widely to benchmark the performance of aerosol optical spectroscopy instruments (Cotterell et al. 2020; Davies et al. 2018; Langridge et al. 2016; Cappa et al. 2008), CA often used as a proxy for oxidized atmospheric aerosol (Choczynski et al. 2021; Marshall et al. 2016; Murray 2008), and PEG used to calibrate and compare instruments for aerosol volatility measurements (Bannan et al. 2019; Krieger et al. 2018; Mason et al. 2015). We decided to use AA after observing strong dependencies of $\rho_e$ for mixed particles on nigrosin concentration. We postulated that this behavior could arise from strong polar interactions attributed to the aromatic groups reported to be present in nigrosin dye (Sedlacek and Lee 2007). AA contains a substituted furan group (an aromatic five-membered ring) and was an ideal system to further examine whether the presence of aromatic groups induced strong changes in effective density. Moreover, our choices of organic systems were constrained by the requirement that the sizes of the studied particles did not change appreciably between aerodynamic classification and subsequent measurement of mobility diameter distributions. If particles were to lose mass by evaporation of volatile components on the timescale of our measurements, negative biases in the measured $d_m$ would arise that would result in overestimation of the effective density. Nig, CA, and AA are all solid powders at room temperature and therefore were assumed involatile, whereas PEG-400 is a liquid with a vapor pressure within the range 10$^{-4}$–10$^{-7}$ Pa (Bannan et al. 2019). We examine below whether there is any impact of the small levels of mass loss expected for PEG on the accuracy of our retrieved effective densities.

4. Results and discussion

4.1. Accuracy and precision of density retrievals

Here, we explore measurements of densities for involatile solid particles for a range of pure (non-
mixed) organic and inorganic species that do not adopt voided structures, and we compare our measured $\rho_c$ against best measurements of corresponding material densities. We examine the impact of a range of factors on the accuracy of effective density retrievals, including the uncertainties in $d_{ae}$ and $d_m$, the parameterization of the Cunningham slip correction, and the impact of particle volatility. There has previously been only a limited assessment of the precision and accuracy of effective density retrievals using the AAC-SMPS approach by Tavakoli and Olfert (2014), who reported values of $0.903 \pm 0.090$ g cm$^{-3}$ for spherical droplets comprised of dioctyl sebacate, a liquid, which differed from the material density ($0.913 \pm 0.003$ g cm$^{-3}$) by only 1%.

4.1.1. Example measurement data and analysis considerations

Figure 2 shows examples of SMPS-measured mobility diameter distributions for AS particles classified by the AAC for various values of $d_{ae}$. Multiple peaks are observed in these distributions, which are particularly noticeable at higher values of $d_{ae}$; for example, three distinct peaks in $d_m$ are observed when $d_{ae} \geq 300$ nm. These peaks are attributed to particles that acquired multiple units of electric charge in the X-ray neutralizer. The charge distribution imparted to the aerosol sample passing through the neutralizer is Boltzmann-like, with charged particles with one unit of charge ($q = 1$) having a higher probability than higher levels of charge ($q = 2, 3$, etc.). Therefore, the peak with the largest amplitude for a given $d_{ae}$ in Figure 2 occurs at the mobility diameter for the particles with $q = 1$ that are of interest for our density calculations.

Importantly, the peaks attributed to multiple charging are observed even though the multiple charge correction was applied in the TSI SMPS software. To demonstrate that the observed peaks are indeed due to multiple charging, we calculated the modal diameter for the $q = 2$ particles ($d_{m,q=2}$) based on the

Figure 2. Example mobility diameter distributions for dry, AAC-selected AS particles. The aerodynamic diameter $d_{ae}$ selected by the AAC is indicated in each plot. The black circles are the measured concentrations at a given mobility diameter, while the red lines are the best fit of a bimodal lognormal size distribution to the measured data.
observed modal mobility diameter for the $q=1$ particles ($d_{m,q=1}$). As the mobility of a particle is directly proportional to the product of the charge on the particle and the Cunningham correction, and inversely proportional to the diameter (Stolzenburg and McMurry 2008), the mobility diameter $d_{q=2}$ of a particle with two elementary charges that has the same geometric diameter of a particle with mobility diameter $d_{q=1}$ with a single elementary charge satisfies the equation $C_c(d_{q=2})/d_{q=2} = 2 C_c(d_{q=1})/d_{q=1}$. For the same mobility spectra shown in Figure 2, we compare the observed $d_{q=2}$ with our calculated values in Figure 3a. This comparison shows excellent agreement, demonstrating that the SMPS-measured peaks at lower diameters result from multiply charged particles.

The presence of these multiple peaks in our mobility spectra indicates issues with the multiple charge correction algorithm implemented by TSI, possibly because the aerosol charging model applicable to X-ray neutralization may not be characterized accurately. The characterization of the charge distribution for X-ray neutralizers, first provided by Tigges et al. (2015b), has been shown to be dependent on operational conditions such as carrier gas, sample flow rate, RH, and the dielectric properties of the particles (Leppä et al. 2017; Tigges et al. 2015a). Indeed, our previous work has demonstrated issues with the charge model for X-ray neutralizers using another TSI classifier available in our laboratory (Cotterell et al. 2020). In this previous work, we reported that the measured optical properties for mobility-classified laboratory generated particles (as determined through high accuracy measurements using cavity ring-down and photoacoustic spectroscopy) could be reconciled with optical modeling predictions only through numerical optimization of the aerosol charge distribution that led to a different distribution required from that recommended by Tigges et al. The charging artifacts introduced by inaccuracies in the representation of X-ray neutralizer charging distributions are probably not commonly observed by many SMPS users who are looking at polydisperse samples, where the impacts of multiple-charge correction errors are not immediately obvious. Nevertheless, SMPS users should be aware of the potential for multiple-charge artifacts to introduce uncertainties and biases in their measurements even when applying the manufacturer’s multiple-charge correction.

The presence of multiple charge peaks was inconsequential to our effective density retrievals. Simply, we took the diameters for $d_{q=1}$ peaks in our mobility spectra. As described in Sect. 3, these mobility diameters were calculated from the mode-average diameters for the full spectrum (with the $q=1$ peaks having the largest amplitude), but we also assess in Sect. 4.1.2 whether using a different determination of the peak diameters (taking the $d_{m,q=1}$ diameter of the $q=1$ peaks as determined from the best fits of bimodal lognormal distributions) impacts the retrieved effective densities. As an example of the subsequent regression for the retrieval of effective density, Figure 3b shows the distribution in measured $d_{m}^2 C_c(d_m)$ versus $d_{ae}^2 C_c(d_{ae})$ for the same measurement data set summarized in Figure 2. The linear regression of this
distribution, constrained through the origin, has a slope that is the inverse of \( \rho_e \) as shown by Equation (4). In this example, the effective density of pure AS particles was found to be 1.808 ± 0.008 g cm\(^{-3} \), with the uncertainty corresponding to the standard error in the slope. When repeat measurements were performed at some compositions, all measurement data for a given composition were aggregated and a single regression to all data was performed to retrieve the effective density. For pure AS particles, we performed one further repeat and the retrieved effective density from the combined regression was 1.808 ± 0.009 g cm\(^{-3} \), which agrees with the material density of 1.77 g cm\(^{-3} \) (Table 1) to within 2%.

### 4.1.2. Accuracy of density retrievals

One source of bias in our effective density retrievals is the determination of \( d_m \) (for the \( q = 1 \) particles) from measured mobility spectra. The systematic errors in measured mobility diameters directly connected to errors in the DMA sheath and excess air flow rates, geometric dimensions of the DMA, Cunningham slip correction, DMA voltage, and the measured sample pressure and temperature were assessed by Kinney et al. (1991). In their work, the authors assessed the systematic uncertainty in \( d_m \) to be ±3.0%. Propagating this level of systematic uncertainty in \( d_m \) through Equation (4) indicates that the corresponding uncertainty in our derived \( \rho_e \) is 4.2%. In addition to these systematic errors, biases could arise in the mode-average diameter from noise in the measured aerosol number concentrations and the discretized distribution in mobility diameters. An alternative approach to determine \( d_m \) that mitigates against the impacts of CPC counting noise and allows determination of a continuous distribution in mobility, and therefore a precise determination of peak diameter, is to fit the mobility distributions to a multimodal lognormal distribution. We found that fitting our distributions to a bimodal lognormal distribution was sufficient to prevent biasing of the best fit distribution to the \( q = 1 \) mode, although inconsequential biases in the fit to \( q = 2 \) peaks are evident in Figure 2 when \( q = 3 \) peaks occur. We contrast the effective densities retrieved when using either the modal diameter calculated from a mode-average of the measured mobility spectra or the diameter \( d_{m-fit} \) for the \( q = 1 \) mode calculated from the best fit of a bimodal lognormal distribution.

Figure S1 in the supplementary information (SI) compares effective densities determined using these two mobility diameter attribution methods and shows that, on average for all 147 particle values determined in this work, the density obtained when using the mode-average diameter is ~0.8% lower than that obtained using the \( d_{m-fit} \) diameter from the bimodal lognormal fit. This level of bias in \( \rho_e \) is lower than the 4.2% standard error in \( \rho_e \) expected to be introduced from the aforementioned systematic errors involved in differential mobility analysis as assessed by Kinney et al. (1991). The main figures and tables presented in this article all report effective densities using mode-average mobility diameters, but corresponding figures using the \( d_{m-fit} \) mobility diameters are provided in the Supporting Information for completeness.

Any bias in the values of AAC-selected \( d_{ae} \) would constitute another source of systematic uncertainty in our retrieved effective densities. Traceable biases would result from uncertainties in the angular frequency of the AAC rotation, the internal dimensions of the AAC cylinders, the sheath flow rate, the description of the Cunningham slip factor, and the value for air viscosity (see Equations (1) and (19) in Tavakoli and Olfert (2013)). Immediately prior to this measurement campaign, our AAC was calibrated by the manufacturer, using a laser tachometer to ensure that the AAC rotational speed was within 1% of the specified value and a Gilibrator (Sensodyne) to ensure the sheath flow rate was within 2% of its specified.

### Table 1. Comparison of \( \rho_e \) from our measurements on pure components with \( \rho_{bulk} \) values reported in the literature. The quoted errors in measured \( \rho_e \) represent the standard error in the density arising from our regression analysis.

| Chemical species       | Measured \( \rho_e/\text{g cm}^{-3} \) | Literature \( \rho_{bulk}/\text{g cm}^{-3} \) | \( 100 \times (\rho_e - \rho_{bulk})/\rho_{bulk} \) |
|------------------------|--------------------------------------|---------------------------------------------|--------------------------------------------------|
| Ammonium sulfate (AS) | 1.804 ± 0.009                        | 1.765-1.772                                 | +1.3 → +2.7                                      |
| Sodium nitrate (SN)    | 2.187 ± 0.042                        | 2.259-2.261                                 | −1.3 → −5.1                                     |
| Sodium chloride (SC)   | 2.061 ± 0.015                        | 2.161-2.164                                 | −3.9 → −5.5                                     |
| Nigrosin dye (Nig)     | 1.632 ± 0.016                        | 1.34-1.60                                   | +1.0 → +23.0                                    |
| Citric acid (CA)       | 1.688 ± 0.022                        | 1.655                                       | +0.1 → +2.7                                     |
| Polyethylene glycol 400 (PEG) | 1.240 ± 0.009 | 1.122-1.126                                | +9.3 → +11.3                                    |
| Ascorbic acid (AA)     | 1.702 ± 0.020                        | 1.694                                       | −0.7 → −1.7                                     |

The quoted ranges in the percentage difference between our measured \( \rho_e \) and the literature density values arise from the standard error in our retrieved \( \rho_e \) and the range in reported literature density values. [1] Tutton (1906); [2] Johnston and Adams (1912); [3] Kracek (1931); [4] Robie et al. (1967); [5] Swanson et al. (1956); [6] Baxter and Wallace (1916); [7] Johnston and Hutchison (1942); [8] Moteki et al. (2010); [9] Radney and Zangmeister (2015); [10] Radney and Zangmeister (2018); [11] Bennett and Yuill (1935); [12] Rodriguez et al. (2012); [13] Sequeira et al. (2019); [14] Sonnergaard (2000).
flow rate. We assumed that the internal dimensions of the AAC classifier (length and radii) are known to within 0.5 mm of the values specified by the manufacturer, the Cunningham slip factor is known to within 2.5% (see below), and the viscosity of air is known to within ±1.3% given typical variations in the temperature of our laboratory during experiments. Assuming these uncertainties, we used standard propagation of error to estimate that the uncertainty in \( d_{ae} \) is \( \sim 1.9\% \), which corresponds to a systematic error in effective density of \( \sim 3.8\% \).

We investigated the magnitude of the uncertainty that arises from using different formulations of the Cunningham slip correction factor. We used the Cunningham slip correction described by Davies (1945) for spherical particles to determine the effective densities according to Equation (4). However, we recognize that there are many reported parameterizations of the Cunningham slip factor, and more recent parameterizations are available, such as those of Allen and Raabe (1985) and Kim et al. (2005), which have both been adopted widely by the aerosol science community. The Davies parameterization gives a Cunningham slip correction factor that is, on average, 2.5% larger than the other parameterizations over the diameter range 50 – 500 nm that is relevant to our work, and the retrieved effective densities using the Davies parametrization are approximately 0.3% less than the values calculated using the other parameterizations. Importantly, these differences are less than the precision in our regressed \( \rho_{e} \).

Using the same approach as Johnson et al. (2020) in combination with our estimated uncertainty of 1.9% in \( d_{ae} \) and of up to 3.0% in \( d_{in} \), we estimate the overall accuracy in \( \rho_{e} \) retrieved using Equation (4) is 7.1%. This estimation approach ignores the small contribution from the Cunningham slip correction factor. As we show below, this estimate of 5.2% is near-identical to the better-than 5% agreement between our measured \( \rho_{e} \) for single component particles with literature values for material density.

The determination of effective densities in this work relies on a linear regression consistent with Equation (4), which is valid for particles with size-independent density. Significant bias could be introduced to our retrieved \( \rho_{e} \) if the effective densities are size-dependent. The \( f \)-factor analysis described in Sect. 2 was performed to assess whether there was any size dependence in our measured densities. Figure S2 in the SI shows that the \( f \) factors for all our aerosol mixtures and pure component systems were within ±5% of \( f = 3 \), the value that is expected when the density is size-independent. Therefore, the density is well approximated by the size-independent assumption of our linear regression approach. There is a possibility that the assumption of spherical shape is not valid for our particles and therefore the densities derived by our linear regression would need to be corrected for the particle dynamic shape factors. However, as we now show, our measured effective densities compare well with literature values for material densities, thus indicating that the shapes of our particles are well represented by the spherical assumption.

Table 1 summarizes our measurements of \( \rho_{e} \) for pure component aerosols comprised of the four organic and three inorganic species of interest, and value ranges reported in the literature for the material densities. Except for Nig and AA, we have been careful to include literature values for material densities that use crystallography methods for the solids or an oscillating U-tube for PEG-400 (a liquid), which represent the techniques-of-choice for accurate and precise measurements of crystalline solid and liquid material densities respectively. For the four crystalline structures, the material densities reported in Table 1 correspond to AS in the orthorhombic system, SC in the face center cubic crystal system, SN in the hexagonal crystal family with space group R\( 3c \) (i.e., the most common crystal structure adopted by SN when crystallized from solution), and CA in the monoclinic system. We note that the latter substance is known to form hydrates during the crystallization from bulk solutions, but the material density reported here corresponds to the anhydrous form. Table 1 summarizes the range of percentage differences between our measured \( \rho_{e} \) and the material densities, considering the range of our measurement precision and the range of reported literature values. Our \( \rho_{e} \) values agree with the reported material densities to better than \( \sim 5\% \) for all substances, except for PEG-400 which is discussed further below. We highlight the large range in reported densities for nigrosin, for which there seems to be no consensus (Radney and Zangmeister 2015, 2018; Moteki et al. 2010). There are conflicting reports of the structure and chemical composition of nigrosin, and it is reported to be a mixture of polyanilines manufactured by heating nitrobenzene, aniline, and hydrochloric acid with a metal catalyst, before adding an orange dye to match a specific color index at a wavelength of 550 nm (Sedlacek and Lee 2007b; Bond et al. 1999). Indeed, Sedlacek and Lee (2007) suspected batch-to-batch and manufacturer variability in the properties of nigrosin dye.
Our measured \( \rho_e \) for PEG-400 particles is \( \sim 10\% \) greater than the material density (Table 1). While the other species we have discussed so far are solids at room temperature and can be considered as involatile species, PEG-400 is a liquid and is semi-volatile. The evaporative loss of PEG-400 between aerodynamic selection and characterization of particle mobility could bias our reported \( \rho_e \) in the observed direction by an amount that depends on the saturation vapor pressure of PEG-400 and the time over which evaporation occurs. The volatility of PEG-400 is not well characterized. Indeed, the composition of PEG-400 is not defined precisely, but instead consists of a mixture of polyethylene glycols with an average molecular weight in the range 380 – 420 g mol\(^{-1}\). Mason et al. (2015) reported the evaporation rate for PEG-400 particles with a diameter of \( \sim 3 \mu m \) as being 0.05 nm s\(^{-1}\), corresponding to a vapor pressure of \( 2.9 \times 10^{-4} \) Pa. Logozzo and Preston (2021) reported a vapor pressure of \( \sim 1 \times 10^{-4} \) Pa from measurements on single, optically trapped aerosol particles. Meanwhile, Krieger et al. (2018) performed limited assessments of the temperature-dependent saturation vapor pressures for octaethylene glycol (i.e., a polyethylene glycol with eight repeating units of the ethylene oxide and therefore a molecular weight of 370.4 g mol\(^{-1}\)), with measured values at 300 K ranging from 9.04 \( \times 10^{-7} \) Pa using an electrodynamic balance to 1.6 \( \times 10^{-6} \) Pa using Knudsen effusion mass spectrometry. Such a large range in estimates of single component vapor pressures, spanning several orders of magnitude, is common for semi-volatile organic compounds found commonly in the atmosphere, such as dicarboxylic acids (Bilde et al. 2015; Cai et al. 2015). Based on the volume of tubing between the AAC and classifier, the volume of our DMA column, and the aerosol sample flow rate of 0.3 L min\(^{-1}\), we expect that the aerosol sample spends \( \sim 100 \) s between AAC classification and exiting the mobility classifier (DMA column). Using this time delay with the Maxwell mass flux equation corrected for the transition regime (Cotterell et al. 2014; Krieger et al. 2012; Ray et al. 1989), and assuming a mean molecular weight of 400 g mol\(^{-1}\) and a diffusion coefficient for PEG-400 in air equivalent to that for octaethylene glycol (3.68 \( \times 10^{-6} \) m\(^2\) s\(^{-1}\), Krieger et al. (2018)), we can reconcile our measured \( \rho_e \) with the literature reported material density if the PEG-400 saturation vapor pressure is \( \sim 1.3 \times 10^{-4} \) Pa. This value is reasonable and lies within the aforementioned range of available literature data. We note that this analysis does not account for evaporation within the AAC instrument, which will bias high our estimated \( d_{ae} \) based on the user selected value. Nonetheless, this discussion serves to highlight that the difference between our measured \( \rho_e \) and material density for PEG-400 is likely caused by evaporation of the semi-volatile PEG between aerodynamic selection and characterization of the mobility diameter. Others should consider the limitations of particle characterizations using the AAC-SMPS approach when examining particles containing volatile components and care should be taken to ensure the impacts of volatility are accounted for or mitigated.

With the exception of PEG-400, the agreement between our measured \( \rho_e \) and reported material densities to better than \( \sim 5\% \) is confirmation that the aerodynamic behavior of our particles is well represented by models that assume a spherical shape and do not contain internal voids that would otherwise lower the effective density, and therefore the dynamic shape factors for these particles are well represented by the assumption \( \chi = 1 \). The formation of spherical particles in our experiments is not unexpected, even for sodium chloride which has a face-center cubic crystal structure in the solid state. The spherical surface of an aqueous aerosol droplet can act as a template for crystal formation upon efflorescence (Hardy et al. 2021; Baldelli and Vehring 2016). Moreover, studies suggest that the drying of droplets with sub-micrometer diameters are more likely to form spherical particles than larger droplets. For example, Baldelli and Vehring (2016) report that aqueous SN droplets with sub-micrometer diameters dried to form spherical particles with high reproducibility, while larger particles adopted morphologies with higher surface roughness. The agreement between \( \rho_e \) and the material densities also indicate that the assumption that our particles are dry is reasonable. However, we cannot rule out entirely the possibility that all the generated particles are devoid of water; for example, macroscopic samples of CA crystallize to their mono-hydrate form when dried at temperatures below 34°C (Lafontaine et al. 2013). It is also important to recognize that Table 1 provides the material densities for crystalline AS, SC, SN and CA; we are not able to confirm the presence or absence of amorphous domains in our generated particles, which may alter the measured effective densities.

### 4.1.3. Precision of density retrievals

The mean precision in the effective density, \( \sigma_{\rho_e} \), determined from the standard errors in the regression slopes for all 147 density retrievals performed in this work, including both pure and internally mixed
particles, is 0.019 g cm$^{-3}$ (or ±1.10%) when using the mode-average calculated $d_{m}$ and 0.016 g cm$^{-3}$ (±0.94%) when using the $d_{m-fit}$ from our bimodal log-normal fits. The higher precision is expected for the latter approach as it mitigates against the presence of noise in the measured mobility size distributions. The correlation between $\sigma_{p}$ and $\rho_{e}$ is weak, with Pearson correlation coefficients of 0.32 and 0.13 when using the mode-average $d_{m}$ and $d_{m-fit}$ mobility diameters, respectively. We highlight that these estimates of $\sigma_{p}$ are better than that in the initial assessment of Tavakoli and Olfert (2014), who reported a measurement precision of 0.090 g cm$^{-3}$ (or ±10.0%) from AAC-SMPS measurements of dioctyl sebacate droplets. Tavakoli et al. determined effective densities from measurements of $d_{m}$ for single values of $d_{ae}$ rather than applying a regression to a distribution in $d_{m}$ with $d_{ae}$ as is done in our work; indeed, if we repeat our density retrievals but use the same single measurement approach used by Tavakoli et al., the standard deviation in our measured $\rho_{e}$ increases by approximately six-fold. Further differences may arise from differences in the stability and magnitude in particle number concentrations generated, which will impact the signal-to-noise ratio in measured mobility diameter spectra.

### 4.2. Density measurements for two-component organic-inorganic aerosol mixtures

We now consider our measurements of $\rho_{e}$ for internally mixed particles consisting of two-component organic-inorganic mixtures. Figure 4 shows our measured $\rho_{e}$ distributions as functions of $w_{org}$. Importantly, Figure 4 shows that the trends in density with $w_{org}$ are characterized sensitively, with the range in measured densities for a given mixture exceeding the measurement sensitivity. We also highlight that the bias of +10% in $\rho_{e}$ for pure component PEG particles, as assessed in Sect. 4.1.2, is small compared to the density variation over the entire range of $w_{org}$. Almost all our mixtures demonstrate variations in $\rho_{e}$ with $w_{org}$ that deviate significantly from ideal mixing predictions. The mixtures involving nigrosin demonstrate particularly large deviations from what would be predicted from a simple ideal mixing rule, with $\rho_{e}$ varying in a non-monotonic manner when Nig is mixed with any of our three inorganic salts.

Although, in principle, the observed deviations in $\rho_{e}$ from ideal mixing could arise from deviations in the dynamic shape factor from $\chi = 1$ (see discussion in Sect. 2), there are several reasons why we do not expect such deviations to occur. First, Sect. 4.1.2 shown that the measured $\rho_{e}$ for single component particles were in excellent agreement with best estimates of material densities available in the literature, indicating $\chi = 1$, although we acknowledge that this assessment does not necessarily pertain to particles when internally mixed. Second, the $\rho_{e}$ in Figure 4 show both positive and negative deviations from the expectation of ideal mixing; if the positive deviations were attributable to changes in particle shape, $\chi$ would have to be less than unity to reconcile the measured $\rho_{e}$ with ideal mixing, yet $\chi$ is almost always greater than one for non-spherical particles (DeCarlo et al. 2004). The analysis below therefore assumes our sampled particles are spherical and that deviations in $\rho_{e}$ from ideal mixing arises from the effects of non-ideal interactions between mixing species, but we acknowledge that the potential for impacts of particle shape cannot be ruled out completely. For mixtures of SN with either CA or AA, a further factor that could impact on measurements of $\rho_{e}$, and cause differences with respect to ideal mixing predictions, is the evaporative loss of nitrate (as HNO$_{3}$) upon particle drying (Wang and Laskin 2014). However, we are not concerned with this evaporative loss given the relative timescales of our measurements following particle drying (~2 min) and those of the loss of nitrate in typical dry particles of SN internally with organic acids; Wang and Laskin (2014) showed that the characteristic timescale for ~50% of the nitrate to be lost by evaporation, from SN particles internally mixed with a range of organic acids, to be ~4 weeks. Moreover, as we shown in Sect. 4.1.2 for measurements on semi-volatile PEG-400 particles, the impacts of significant evaporation of particle mass between AAC selection and mobility characterization would manifest as a consistent positive bias in $\rho_{e}$ from the ideal mixing prediction. Yet, this effect was only moderate for PEG-400. For mixtures of SN with either CA or AA, positive deviations in $\rho_{e}$ from ideal mixing are observed for some mixture compositions with CA, but only negative deviations are observed for mixtures with AA. Therefore, the impacts of acidity on the evaporation of nitrate are negligible on the timescales of our measurements.

We now investigate the representation of our measured $\rho_{e}$ for organic-inorganic mixtures by mixing rule models. In the following, we first derive an expression for the mixture density that considers only ideal mixing. Next, we modify the ideal mixing expression to include a correction that accounts for non-ideal interactions between the organic and inorganic species. We
fit this model to our measured density distributions in the mass-fraction domain to assess the particle volume change on mixing and the deviations in the mixture densities from ideal mixing. We repeat these comparisons when fitting our non-ideal mixing model in the mole-fraction domain.

4.2.1. The ideal mixing rule for predicting the densities of mixtures

We consider the mixing of species with known mass fractions $w_i$. The ideal mixing rule for density assumes that the total volume of a mixture is the sum of the individual volumes and is given by:
\[
\rho_{\text{ideal}} = \frac{m}{V} = \frac{\sum m_i}{\sum \rho_i w_i} = \frac{1}{\sum \rho_i w_i}
\]

in which \(m\) and \(V\) are the total mass and volume of the mixture, respectively, and \(m_i\), \(\rho_i\) and \(w_i\) are the mass, density, and mass fraction of component \(i\) respectively. We have chosen to represent the ideal mixing rule in terms of mass fraction because we control (measure) the component mass fractions when we formulate our aqueous solutions for nebulization. For our two-component organic-inorganic mixtures with an organic mass fraction \(w_{\text{org}}\) and an inorganic mass fraction \(w_{\text{inorg}} = 1 - w_{\text{org}}\):

\[
\rho_{\text{ideal}} = \frac{w_{\text{org}}}{\rho_{\text{org}}} + \frac{(1-w_{\text{org}})}{\rho_{\text{inorg}}}
\]

(9)

in which \(\rho_{\text{org}}\) and \(\rho_{\text{inorg}}\) are the pure component densities of the organic and inorganic species, respectively. These two pure component densities are varied using the same least squares fitting method described in Sect. 4.2.2, and the results of these fits are shown in Figure 4.

4.2.2. Non-ideal mixing in the mass-fraction domain

Equation 9 assumes ideal mixing in that the total mass is the sum of the individual masses and the total volume is the sum of the individual volumes of the components \((m_i/\rho_i)\). Although the total mass is always conserved, most chemical systems exhibit non-ideal mixing in which the total volume is not. Therefore, we modify Equation (9) by adding a term that describes the change in the total volume of the system due to non-ideal mixing:

\[
\rho_{\text{mix}} = \frac{1}{\rho_{\text{org}}} + \frac{(1-w_{\text{org}})}{\rho_{\text{inorg}}} + V_M
\]

(10)

in which \(V_M\) is a mass-normalized volume change on mixing, which depends on \(w_{\text{org}}\). The functional form of \(V_M\) must recognize that \(V_M = 0\) in the limits \(w_{\text{org}} = 0\) and \(w_{\text{org}} = 1\); i.e., there is no volume change on mixing when the generated particles are composed of either the pure organic or inorganic species. Such a functional form can be represented by a polynomial expansion in which each factor contains the term \(w_{\text{org}}(1-w_{\text{org}})\). Redlich and Kister (1948) proposed a polynomial expansion that is commonly used to describe excess thermodynamic properties for mixtures (Zardini et al. 2010; Singh et al. 2009). We therefore use the Redlich-Kister polynomial expansion and write \(V_M\) as:

\[
V_M = w_{\text{org}}(1-w_{\text{org}}) \sum_{k=0}^{n} L_k (2w_{\text{org}} - 1)^k
\]

(11)

in which \(L_k\) is the Redlich-Kister (RK) coefficient for polynomial order \(k\). The model described by Equations (10) and (11) for mixture density \(\rho_{\text{mix}}\) was fitted to our measured effective densities \(\rho_e\) by varying the parameters \(\rho_{\text{org}}\), \(\rho_{\text{inorg}}\), and the polynomial coefficients \(L_k\) such that the sums of the weighted least-squares residuals:

\[
R = \sum_i \left( \frac{\rho_{i,e} - \rho_{i,\text{mix}}}{\rho_{i,e}^2} \right)^2
\]

(12)

were minimized, with \(\rho_{i,e}\) and \(\rho_{i,\text{mix}}\) the measured and modeled densities, respectively, at an organic mass fraction \(w_{\text{org},i}\) and the summation is over all \(i\) measured effective density values. We experimented with different versions of this merit function, experimenting also with versions of Equation (12) where no weighting for the measured density is included, or weighting instead for the uncertainty (standard error) in the measured \(\rho_e\), but we found that the choice of merit function was of little consequence in reducing the fit residuals between our measured \(\rho_e\) and the best-fit non-ideal mixing model. To mitigate against biasing our fit to regions of \(w_{\text{org}}\) where repeat measurements of \(\rho_e\) were made (open squares in Figure 4), we fit our model to the \(\rho_e\) derived from the regression of all repeat data at a given \(w_{\text{org}}\) (filled circles in Figure 4). We truncated Equation (11) at \(n = 2\), beyond which there was little improvement in the model fit to measured \(\rho_e\) as discussed below.

Figure 4 shows the best fits of Equations (10) and (11) to our measured \(\rho_e\) with the best fit parameters for these curves summarized in Table 2. The corresponding best fit \(V_M\) distributions are shown in Figure 5, which are compared against measured \(V_M\) values determined from the difference between our measured \(\rho_e^{-1}\) and calculated \(\rho_{\text{ideal}}\). Figure 5 clearly

| Mixture | \(\rho_{\text{org}}\) / (g cm\(^{-3}\)) | \(\rho_{\text{inorg}}\) / (g cm\(^{-3}\)) | \(L_0\) / (cm\(^{3}\) g\(^{-1}\)) | \(L_1\) / (cm\(^{3}\) g\(^{-1}\)) | \(L_2\) / (cm\(^{3}\) g\(^{-1}\)) |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|
| AS-Nig  | 1.606           | 1.815           | 0.572           | -0.304          | -1.003          |
| SN-Nig  | 1.614           | 2.237           | 1.022           | -0.473          | 0.041           |
| SC-Nig  | 1.596           | 2.046           | 0.486           | -0.246          | -0.764          |
| AS-CA   | 1.688           | 1.810           | 0.014           | 0.006           | -0.032          |
| SN-CA   | 1.698           | 2.166           | -0.060          | 0.140           | 0.031           |
| SC-CA   | 1.674           | 2.050           | -0.094          | 0.036           | 0.091           |
| AS-PEG  | 1.239           | 1.808           | -0.076          | 0.035           | -0.083          |
| SN-PEG  | 1.245           | 2.175           | -0.061          | -0.110          | 0.150           |
| SC-PEG  | 1.236           | 2.080           | -0.075          | 0.031           | -0.245          |
| AS-AA   | 1.685           | 1.795           | 0.055           | 0.162           | -0.146          |
| SN-AA   | 1.705           | 2.161           | -0.027          | -0.100          | 0.315           |
| SC-AA   | 1.685           | 2.061           | -0.101          | 0.065           | -0.110          |

The optimal densities of the organic and inorganic species from our best fits of our non-ideal mixing model are denoted \(\rho_{\text{org}}\) and \(\rho_{\text{inorg}}\), respectively, to distinguish these values from our measured values specified in Table 1 that are more robust estimates of the pure component densities.
demonstrates the convergence of our best-fit $V_M$ to our measured values as Equation (11) is truncated at ever higher values of $n$. We find that truncating Equation (11) at $n = 2$ is optimal for capturing the measured trends in $V_M$; comparison when including higher order RK polynomial terms (see Figures S5 and S6 in the SI) leads to trends that are unlikely to reflect true physical changes in $V_M$ and for which the improvement in the least square residual (Equation (12)) is only marginal. $V_M$ takes large values for some mixture compositions that involve Nig, with values as large as 0.15 cm$^3$ g$^{-1}$ for mixtures of AS or SC with
Figure 6. The relative difference in density, $\delta \rho$, between the best-fit $\rho_{\text{mix}}$ from our non-ideal mixing model (Equations (10) and (11)) and the corresponding ideal mixing rule for density (Equation (9)) calculated using Equation (13), plotted as a function of organic mass fraction, $w_{\text{org}}$ for the each of the different organic-inorganic mixtures investigated. The corresponding $\delta \rho$ between the measured $\rho_e$ values and the ideal mixing rule are also shown, with values for AS, SN and SC mixtures shown by square, diamond, and triangle symbols respectively. Note that the vertical scale for (a) is different to that of the other plots.
Nig. Meanwhile, for mixtures with other organics, values of $V_M$ are substantially less. Indeed, $V_M$ is negligible for AS-CA mixtures, with deviations less than 0.01 cm$^3$ g$^{-1}$ that are within the noise of measured $V_M$; thus, mixed AS-CA particles can be considered as ideal mixtures. Although Figure 4 might be interpreted as showing that the PEG mixtures behave almost ideally, Figure 5 clearly shows that the deviations from ideality in terms of $V_M$ for these PEG mixtures are comparable to those for the other organic-inorganic mixtures studied (excluding AS-CA and those involving Nig).

Figure 6 summarizes the relative deviations in the best-fit $\rho_{mix}$ from $\rho_{ideal}$ calculated as:

$$\delta \rho = \frac{\rho_{mix} - \rho_{ideal}}{\rho_{ideal}} \times 100\%$$  \hspace{1cm} (13)

The measured densities deviate from that predicted using an ideal mixing rule model by as much as 20% for mixtures with Nig, compared to no more than 7% for the other mixtures considered. Similarly, Figure S9 shows that the volumes of mixing for mixtures with Nig can be 20–30% of the volumes calculated from ideal mixing contributions, whereas these volumes are no more than 6% for mixtures with the other organic species.

Understanding the trends in non-ideal behavior for mixtures, in general, requires insight into the structure of the material constituting the particle. For example, the organic and inorganic species that, in their pure form, adopt crystalline structures, may form completely different structures when mixed with each other. Even for mixtures of CA in its monohydrate form (which is likely formed following drying at 293 K) and AS, both of which adopt orthorhombic crystal structures (Lafontaine et al. 2013; Okaya et al. 1958), it is not possible to infer straightforwardly the crystal structures; the interactions between CA and the inorganic ions ($\text{NH}_4^+$, $\text{SO}_4^-$) will be different compared to those between like-species. Even if CA-AS mixtures do crystallize in the orthorhombic system, the unit cell dimensions (therefore deviations from ideal mixture density) are likely different, depending on the strength of the interactions between dissimilar species. Therefore, we cannot predict whether a particular mixture will deviate (and how much by) from ideality based on crystal structure information for pure components. More broadly, we do not have information from this study on whether our particles can be considered as homogeneous, or phase separated.

The specific causes of the highly non-ideal behavior of $\rho_e$ for mixtures containing Nig are unclear. We highlight that the structure and composition of nigrosin dye is not known precisely. For example, Hasenkopf et al. (2010) state that the dye has the chemical formula $\text{C}_{43}\text{H}_{20}\text{N}_7\text{S}_3\text{O}_{18}$ which has a molecular weight of 1090.92 g mol$^{-1}$. Meanwhile, several papers report a chemical formula of $\text{C}_{48}\text{N}_9\text{H}_{51}$, which has the molecular weight 753.98 g mol$^{-1}$ (Wiegand et al. 2014; Lack et al. 2006; Bond et al. 1999). Furthermore, the manufacturer for the batch of dye used in our experiments (Sigma-Aldrich) states a molecular weight of 202.21 g mol$^{-1}$ on their safety data sheet but no chemical formula. Sedlacek and Lee (2007a) describe nigrosin as a mixture of polyaniline pigments with an orange dye. One hypothesis is that the non-ideal behavior for Nig mixtures arises from steric effects, with nigrosin dye containing species with higher molecular weights compared to the inorganic species considered. PEG-400 also has a high molecular weight (380–420 g mol$^{-1}$) that is probably comparable to that of Nig, but the deviations in $\rho_e$ for PEG mixtures are much less. However, consideration of molecular weight alone does not form a comprehensive assessment of steric effects, as this ignores potential differences in conformational flexibility such as rotational degrees of freedom for the PEG polymeric chains that may be absent in nigrosin species. A second hypothesis is that the aromaticity of the polyaniline species purported to constitute nigrosin dye might strongly influence the intermolecular interactions in the Nig mixtures. However, AA contains a furan ring and yet its mixtures demonstrate relatively mild deviations in $\rho_e$ from ideality, although this observation does not directly exclude the role of the different phenyl aromatic groups that are likely present in nigrosin species in perturbing the volume of mixing.

**4.2.3. Non-ideal mixing in the mole fraction domain**

The representation of non-ideal mixing in terms of the mass fractions of mixture components can be advantageous because, in our experiments, the masses of individual components are measured directly. This knowledge of mass composition is commonplace in laboratory and field experiments, such as studies that use mass spectrometry. However, the interactions that drive non-ideal mixing occur between molecules and are not physically dependent on masses. Mixtures of two species with equal mass can correspond to vastly different numbers of moles of the two components, depending on their molecular weights. For example, a 1:1 mass mixing ratio of SC:PEG corresponds to a ~7:1 mole ratio. Therefore, we now consider the
representation of \( \rho_{\text{mix}} \) in the more physically based mole-fraction domain for all mixtures except those containing nigrosin, as its molecular weight is not known. Although we noted in Section 4.1.2 that the molecular weight of PEG-400 is not known exactly, it is much more constrained (to within \( \sim 5\% \)) than that of nigrosin, and therefore it is reasonable to include densities of the PEG mixtures in the mole-fraction domain.

The ideal mixing rule presented in Equation (9) for \( \rho_{\text{ideal}} \) in terms of mass fractions of the organic species (\( w_{\text{org}} \)) can be transformed to an expression in terms of mole fractions of the organic species (\( x_{\text{org}} \)):

\[
\rho_{\text{ideal}} = \frac{1}{\rho_{\text{org}}} \left( \frac{1}{x_{\text{org}}M_w + (1-x_{\text{org}})M_{\text{inorg}}} \right) + \frac{1}{\rho_{\text{org}}} \left( \frac{x_{\text{org}}M_w + (1-x_{\text{org}})M_{\text{inorg}}} {x_{\text{org}}M_w + (1-x_{\text{org}})M_{\text{inorg}}} \right)
\]

\[\text{(14)}\]

in which \( M_{w,\text{org}} \) and \( M_{w,\text{inorg}} \) are the molecular weights of the organic and inorganic species, respectively. The expression for mixture density is then:

\[
\rho_{\text{mix}} = \frac{1}{\rho_{\text{org}}} \left( \frac{1}{x_{\text{org}}M_w + (1-x_{\text{org}})M_{\text{inorg}}} \right) + \frac{1}{\rho_{\text{org}}} \left( \frac{x_{\text{org}}M_w + (1-x_{\text{org}})M_{\text{inorg}}} {x_{\text{org}}M_w + (1-x_{\text{org}})M_{\text{inorg}}} \right) + V_M
\]

\[\text{(15)}\]

for which \( V_M \) is now expressed as an RK polynomial expansion in terms of the mole fraction:

\[
V_M = x_{\text{org}}(1-x_{\text{org}}) \sum_{k=0}^{n} L_k (2x_{\text{org}} - 1)^k
\]

\[\text{(16)}\]

in which \( L_k \) are the best-fit RK polynomial coefficients when fitting in the mole-fraction domain. We stress that, while Equations (9) and (14) are equivalent and represent the ideal mixing rule in terms of the mass and mole fractions, respectively, of the mixing species,
it is important to appreciate that Equations (11) and (16) for \( V_M \) are fundamentally different treatments of the volume of mixing, with the former representing the effects of non-ideal interactions between masses of component species and the latter the effects of interactions between moles of component species. We fit Equations (15) and (16) to our measured densities \( \rho_e \) in the same way as before, varying \( \rho_{org} \), \( \rho_{inorg} \), and \( L_k \) to minimize the sums of the relative least-squares residuals. We note that the best fit \( V_M \) values still have units of \( \text{cm}^3 \ \text{g}^{-1} \) (as can be seen from dimensional analysis of Equation (15)), but it is straightforward to convert \( \text{cm}^3 \ \text{g}^{-1} \) to an excess molar volume with units \( \text{cm}^3 \ \text{mol}^{-1} \) by dividing by the total number of moles in 1 g of the mixture (which varies with mixture composition). Figure 7 compares our measurements of \( \rho_e \) as functions of \( x_{org} \) with the best fits of \( \rho_{mix} \) described by Equations (15) and (16), with the RK polynomial expression truncated at \( n = 2 \) as for our mass mixing comparisons in Sect. 4.2.2. Table 3 summarizes the parameters for the best fits of \( \rho_{mix} \) in the mole fraction domain and the corresponding values of \( V_M \) are shown in Figure S10. Across all nine chemical mixtures for which both the mass- and mole-mixing models were fitted, the mean percentage difference between the measured \( \rho_e \) and the best-fit models for mass- and mole-mixing took similar values of 3.2% and 3.8%, respectively. Moreover, this percentage difference was lower when using mole mixing for some mixtures (SN with CA, and SC with CA), but was lower when using mass mixing for other mixtures. Therefore, we are unable to distinguish any benefit in using the more physically based mole mixing approach to treating non-ideal interactions for our studies on a limited range of organic-inorganic mixtures.

The magnitudes of the excess molar volumes for our nanoparticle solid-solid (and solid-liquid in the case of PEG) mixtures are up to \( 4 \ \text{cm}^3 \ \text{mol}^{-1} \). To the best of our knowledge, little (if any) research has focused on mixture densities for dry, solid particles, although many investigations have reported excess molar volumes for liquids including aqueous solutions (Rodríguez et al. 2012; Clegg and Wexler 2011) and ionic liquids (Singh et al. 2009). Values of \( V_M \) in aqueous solutions and ionic liquids are typically less than \( 1 \ \text{cm}^3 \ \text{mol}^{-1} \), so the excess molar volumes observed in our study indicate appreciable non-ideal mixing in solids.

5. Conclusions

We have applied the AAC-SMPS approach to the determination of effective densities for two-component organic-inorganic mixtures and considered how various factors impacted the accuracy of this determination. Uncertainties in the particle aerodynamic and mobility diameters and differences in formulations of the Cunningham slip correction factor could introduce biases in determined \( \rho_e \) of up to ±3.8%, ±4.2%, and ~0.3%, respectively. An analysis of the particle mass-mobility exponent (\( \beta \)) indicates that \( \rho_e \) is independent of particle size and therefore the assumption of size-independent densities is valid. Importantly, our measured \( \rho_e \) for single component aerosols comprised of nonvolatile (solid) materials agreed to within ~5% of the known material densities available in the literature. Deviations in \( \rho_e \) from known material densities occurred when the particles contained a semi-volatile component; these situations are attributed to reductions in the particle mobility diameters between AAC classification and measurements of the particle mobility diameter distributions due to evaporation. Researchers should take care in ensuring that any impacts of volatility of their aerosol samples are considered if using the AAC-SMPS approach for effective density characterization. Furthermore, we have shown that the precision in our measured \( \rho_e \) values is ~1%.

Our effective density measurements for two-component organic-inorganic mixtures demonstrated substantial deviations from expectations of an ideal mixing model, except for AS-CA mixtures. We utilized two different approaches to modeling the non-ideal mixing for our systems, both of which used Redlich-Kister polynomials to represent the volume change of mixing: one model parameterized the mixing in terms of mass fractions (i.e., it treated the
mixing between component masses), whereas the other model parameterized the mixing in terms of mole fractions (i.e., it treated the mixing between molecules). We could not distinguish any significant difference in the performance of the more physically based mole-mixing approach over the treatment of non-ideal mixing between masses. Ultimately, deviations in density from ideal mixing were up to 20% for mixtures involving nigrosin dye, and up to 7% for those containing the other organics investigated. Excess molar volumes for our dry particles (neglecting those comprising nigrosin) were up to 4 cm$^3$ mol$^{-1}$, which is substantially larger than the excess molar volumes reported for common aqueous or ionic liquid mixtures. The large deviations in $\rho_e$ from ideal mixing reported here likely have great impacts on current common approaches for estimating effective densities from mass spectrometry data, and on predictions of parameters that depend on effective density. The assumption of ideal mixing could introduce considerable biases in predictions of densities, with subsequent impacts on the calculation of aerosol dynamical and optical properties.

Disclosure statement

The authors declare that they have no conflict of interest.

Data availability

For data related to this article, please contact Michael I. Cotterell (m.cotterell@bristol.ac.uk).

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