

On the three charge regimes of bipolar charge conditioners

Robert T. Nishida^{*1,3}, Tyler J. Johnson^{1,2}, and Jason S. Olfert²

¹Atmose Ltd., Edmonton, Alberta, Canada

²Department of Mechanical Engineering. University of Alberta,
Edmonton, Alberta, Canada

³Department of Mechanical and Mechatronics Engineering. University
of Waterloo, Waterloo, Ontario, Canada

January 22, 2025

Abstract

Many aerosol instruments utilize bipolar charge conditioners (neutralizers), including scanning mobility particle sizers (SMPS). The charge distribution from a bipolar charge conditioner must be known to calculate size distributions from SMPS scans. Therefore, a reproducible and known ‘steady-state’ charge distribution is desired to improve measurement accuracy. In this work, we show that although a steady-state charge develops within a common Kr-85 bipolar charge conditioner (TSI 3077A), gaseous ions are readily convected into tubing downstream of the charge conditioner, causing significant deviation from steady-state in less than a second. The ‘downstream ions’ are predominantly positive since negative ions are more readily lost to tubing walls due to their higher diffusivity. Others have previously studied this potential effect, but there is disagreement among them. This study resolves the disagreements, and to the authors’ knowledge, we are the first to: quantify the surprising significance of this effect (mean charge at 239 nm changes by up to a factor of 4); show it occurs rapidly (milliseconds); and demonstrate that a true steady-state distribution is more asymmetric than classical theory (mean charge at 239 nm is $>3\times$ higher in magnitude). Interaction time of the particles with the remaining free ions downstream of the charge conditioner is shown to be the main consideration for this effect, as demonstrated by varying flow rate, tube length and tube diameter and achieving

^{*}Present address: Department of Mechanical and Mechatronics Engineering. University of Waterloo, Ontario, Canada

similar charging results as a function of this time. We perform advanced numerical modelling of charging, convection and diffusion of particles and ions, and show good quantitative agreement with experimental data. These results are further supported by similar charging results measured from a bipolar charge conditioner that has a different internal geometry and ion source than the 3077A charger. To increase consideration of this critical charging effect and enhance understanding of bipolar charging in general, we thereby quantify three distinct regimes of bipolar charging, namely: the 1) charging regime (i.e., as charge develops from its initial to steady-state), 2) steady-state regime, and 3) discharging regime (i.e., effect of ‘downstream ions’). These three regimes of bipolar charging have wide implications for designing instrumentation, interpreting measurements and validating charging models with the aim of improving accuracy in aerosol instruments such as the SMPS.

1 Introduction

Fine particulate matter in polluted air is now the leading environmental risk to health, greater than unsafe water or sanitation (Murray et al., 2020). Due to their climate-forcing potential and complex characteristics, aerosols present a significant source of uncertainty in models of climate change, which are necessary for international climate policy and regulations (Masson-Delmotte et al., 2021).

Accurate quantification of aerosol particles commonly relies on instruments which electrically charge particles for analysis, many of which employ a bipolar charge conditioner (or neutralizer). These instruments include those which characterize particle size distributions with high resolution for regulatory monitoring of ground and air transport emissions and ISO standard atmospheric measurements (Wang and Flagan, 1990; ISO, 2009), as well as low-cost monitors for averaged particle properties in industrial workplaces, indoor air quality and outdoor air pollution in networks of monitors with high spatial and time resolution (Nishida et al., 2020). Furthermore, bipolar charge conditioners are used to bring highly charged aerosols to a near-neutral charge distribution for a range of aerosol applications including evaluation of particle filters (e.g., for masks, respirators, and building filtration systems) and conditioning of aerosol samples prior to regulatory measurements.

A typical bipolar charge conditioner generates ionized gas molecules which subsequently charge or discharge the sampled particles by diffusive and electrostatic forces, resulting in a distribution of positively charged, negatively charged and uncharged particles (Fuchs, 1963; Wiedensohler, 1988). The fraction of total particle concentration at each discrete charge level tends to reach a steady-state charge distribution which is centered near neutral (Hoppel and Frick, 1990).

In the ISO standard method for determining particle size distributions, e.g., using a Scanning Mobility Particle Sizer (ISO, 2009), the charge distribution as a function of particle mobility diameter must be known. In practical applications, the charge distribution is assumed to be known, or estimated in real-time by empirical measurements (Chen and Jiang, 2018; Li et al., 2022), and then applied in the inversion used to convert measured signals to reported particle size distributions. Discrepancies between the true charge distribution and the charge distribution used in the inversion therefore bias the reported size distributions (Leppä et al., 2017; Johnson et al., 2021). For this application, bipolar charging is used in part because the well-defined steady-state charge distribution is achievable, enabling accurate and stable measurements (Flagan, 1998; Vivas et al., 2008). However, most bipolar charge conditioners currently in operation do not account for the effect of ions convected downstream of the charge conditioner and their continued interaction with the particles. Thus, these charge conditioners do not maintain a steady-state charge distribution at their outlet or at the inlet of downstream instrumentation, the location where a steady-state distribution is needed.

This effect was first identified by Hoppel and Frick (1990), who demonstrated numerically and experimentally that ions convected downstream will preferentially lose negative ions due to their higher diffusivity, resulting in a net concentration of posi-

tive ions and positively charging the particles downstream of the charge conditioner. The study called this effect “aerosol charging after the ionization is terminated” and demonstrated experimentally that the negatively to positively charged concentration ratio of particles shifted by a factor of 1.5 as the charger’s length downstream of its ionization region was increased by 17.5 cm, resulting in a 3 s longer residence time. However, more recent studies (Alonso et al., 2001; Lee et al., 2005; He and Dhaniyala, 2014; Johnson et al., 2020), including one with the authors of this study, have disagreed on the significance of this effect (see Section 1.3 for detailed discussion). This disagreement is likely a key reason why most current bipolar charge conditioners do not account for the effect.

While many charge conditioners have been shown to produce charge distributions similar to those predicted in the widely applied study of Wiedensohler (1988), which builds on seminal work from Fuchs (1963) and Hoppel and Frick (1986), these are at specific operating conditions, such as flow rate, pressure, temperature, gas/aerosol composition, charger geometry, and geometry downstream of the ionization region prior to ion removal. The latter is largely not reported, and thus not likely controlled/monitored, in most charging studies. Anecdotally, this may help explain the disagreement and variation in charging results from seemingly similar bipolar charge conditioners summarized by the authors when generating a previous review of bipolar charging measurements (Johnson et al., 2020). This aspect is further convoluted by charging models that do not account for the effect of downstream ions being fit to experimental results that include this effect (likely unknowingly in some cases). This results in a model suitable for that particular charger configuration and operating conditions, but limits applying it to other configurations and conditions without refitting/validation against corresponding experimental results.

Our study resolves these disagreements and discrepancies by clearly demonstrating that interaction time between the particles and remaining free ions downstream of the charge conditioner is the main consideration of this effect. Specifically, the recent studies of the effect of downstream ions (Alonso et al., 2001; Lee et al., 2005; He and Dhaniyala, 2014; Johnson et al., 2020) did not measure the effect on a quick enough timescale (milliseconds) to capture its significance. Therefore, our study agrees with and builds upon Hoppel and Frick’s 1990 work by focusing on this effect and using analytical, numerical and experimental methods to fully demonstrate it and provide critical insights. To improve understanding and clarity, this study also formally defines three distinct regimes of bipolar charging, 1) the charging, 2) steady-state and 3) discharge regimes. The following three subsections provide additional context, including previous work completed, for each of these distinct regimes. These regimes can be used to achieve a desired bipolar charge distribution in new bipolar charge conditioners and particle monitors, thus providing an opportunity to significantly improve the reproducibility and accuracy of bipolar charge distributions

1.1 Charging Regime

A bipolar charge conditioner is commonly operated using an alpha or beta radioactive source (ISO, 2009) or X-ray ionization source (Lee et al., 2005), although, various other ionization sources can be applied (Adachi et al., 1993b; Stommel and Riebel, 2004; Han et al., 2009; Kwon et al., 2006). The charge conditioner first ionizes gas molecules which subsequently transfer charge to the sampled particles by diffusion charging, resulting in a distribution of positively charged, negatively charged and uncharged particles (Fuchs, 1963; Wiedensohler, 1988). To a first approximation, diffusion charging is independent of particle material and does not require an externally applied electric field (Hinds, 1999).

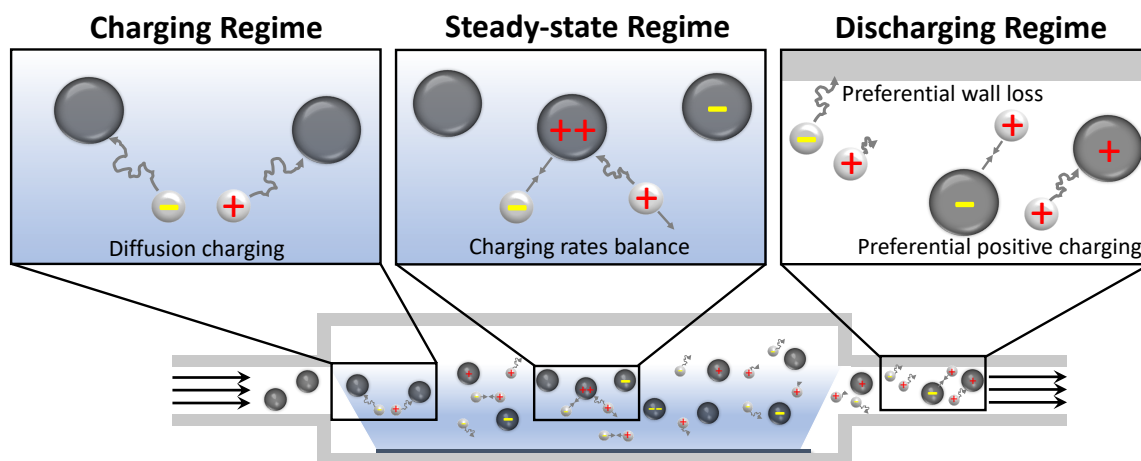


Figure 1: Diagram of a typical bipolar charge conditioner depicting the three charging regimes. Particles (dark grey) are convected through the inlet tubing, charged/discharged by red '+' and negative (yellow '-') gaseous ions (light grey), and convected through the outlet tubing. The ionization region represented by blue shading is the volume in which ions are produced by an ion source.

Figure 1 shows an example bipolar charge conditioner to illustrate the three regimes of bipolar charging. The first panel shows the charging regime during which particles are exposed to ionized gas molecules and during which positive and negative charges are transferred from ions to particles as the charge distribution approaches a steady-state (Adachi et al., 1980). Though Figure 1 shows initially uncharged particles convected into the inlet of the bipolar charge conditioner, even particles with initially high charges will tend towards a steady-state charge distribution in the charging regime (Cooper and Reist, 1973), and the process can occur rapidly (Adachi et al., 1980).

In bipolar charging, the particle charge levels approach a charge distribution centered near neutral (Hopple and Frick, 1986, 1990; Wiedensohler, 1988). For example, as shown in the middle panel of Figure 1, a +2 charged particle is more likely to

combine with a -1 ion than a +1 ion of similar diffusivity due to electrostatic attraction rather than repulsion (Fuchs, 1963). That process is similar for other charge levels, including at lower and higher charge states (Fuchs, 1963). However, particles are increasingly less likely to carry charge at levels further from neutral when ions of both polarities are available for charging (Hoppel and Frick, 1986, 1990; Wiedensohler, 1988). The ion-to-particle charge transfer rates balance across all charge levels as the steady-state charge distribution is established (Fuchs, 1963).

1.2 Steady-state regime

In a bipolar charge conditioner, a steady-state charge distribution is reached after a sufficient interaction time between ions and particles (Hinds, 1999), determined by charger geometry and volumetric flow rate, for example. The middle panel of Figure 1 shows the steady-state regime within the charger during which charging rates have balanced such that the overall charge distribution remains constant. To maintain the steady-state charge, a sufficient number of ions of both polarities relative to particles must remain available for charging (de La Verpilliere et al., 2015; Ibarra et al., 2020; Adachi et al., 1980; Hoppel and Frick, 1990), the ratio of positive-to-negative ion concentrations must be constant (Hoppel and Frick, 1990), and the ions should have constant properties (e.g., mass and mobility). If those conditions are satisfied, the steady-state is then independent of (Hoppel and Frick, 1990; ISO, 2009):

- particle concentration;
- ion concentration¹;
- residence time in charging region; and,
- initial charge state.

Thus, the resulting steady-state charge distribution is primarily a function of particle mobility diameter, at least for spherical particles (Johnson et al., 2020, 2021; Adachi et al., 1980; Kousaka et al., 1983), and insensitive to the parameters listed above. Since parameters such as ion concentration and residence time may be imprecise or vary with time, achieving and maintaining a steady-state charge is attractive for enhancing accuracy and long-term stability in aerosol measurement systems (Vivas et al., 2008; Knutson and Whitby, 1975; Kousaka et al., 1983; Fissan et al., 1983; Ten Brink et al., 1983) as opposed to other charging methods such as unipolar charging, where steady-state is not reached.

In contrast, unipolar charging enables high-intrinsic charge efficiencies relative to bipolar charging, which benefits some applications, but results in less certain charge states as there is no steady-state charge distribution equivalent in practical applications (Intra and Tippayawong, 2011). The net charge transferred to aerosol particles depends directly on the efficacy of the ion source and charger design, i.e., the number of ions generated and time available to transfer charge to particles (White, 1951), though the rate of ion production can be controlled (Liu et al., 1974). The

¹assuming a constant ratio of positive to negative ions

transfer rate of ions to the particles must be known or calibrated for measurement inversions (Kaminski et al., 2012; Fierz et al., 2011; Biskos et al., 2005). Therefore, the accuracy and stability of steady-state bipolar charge distribution are particularly attractive for charge-based measurements.

1.3 Discharging Regime

Though it is self-evident that aerosol particles are convected downstream of bipolar charge conditioners, it is less well known that ions are also readily convected downstream of the charger’s ionization region (where ions are produced by the ionization source) (Johnson et al., 2020). In many cases, this convection of both particles and ions through additional volume (often still referred to as part of a charging region) is intentional to increase the interaction time between the two and lead to a higher likelihood of reaching a steady-state charge distribution (Adachi et al., 1993a). However, this common approach can adversely affect the steady-state charge distribution of the aerosol particles.

The third panel of Figure 1 shows ions convecting into tubing downstream of the ionization region, and depositing on tubing walls by diffusion or continuing to charge particles. Negative ions typically have higher diffusivity than positive ions, and are more readily lost at the charger and tubing walls (Tigges et al., 2015; Hoppel and Frick, 1990; Johnson et al., 2020). Then, a net positive concentration of ions remains in the flow with the particles and shifts the charge distribution more positive relative to its state at the outlet of the ionization region (Hoppel and Frick, 1990; Lee et al., 2005), thereby shifting mean charge more positive as well. By varying volumetric flow rate and downstream tube lengths, the concentrations of positive and negative ions and particle-ion interaction time downstream of the charger are changed (Johnson et al., 2020).

While there has been some prior investigation of the effect of downstream ions by others, there is disagreement between previous studies regarding the effects of these predominantly positive ions downstream of the bipolar charge conditioner on the particle charge fractions. Alonso et al. (2001) concluded that these downstream ions do not affect a charge distribution which has achieved steady-state. He and Dhaniyala (2014) found no significant flowrate dependence for a ^{85}Kr (370 MBq), ^{210}Po (18.5 MBq) or X-ray bipolar charge conditioner, but did find a significant effect on particle charging in a 74 MBq ^{85}Kr bipolar charge conditioner. Tigges et al. (2015) concluded that despite finding ‘non-equilibrium’ (unsteady) charging due to downstream ions, the effect of the free-ions downstream of the charge conditioner is negligible for typical SMPS measurements (<5% change in singly-charged particles).

In contrast, studies have found that preferential diffusion losses of ions of one polarity downstream of the ionization region of the charger will significantly affect the charge distribution of the particles (Hoppel and Frick, 1990; Lee et al., 2005; Johnson et al., 2020). Hoppel and Frick (1990) modelled and measured the ion environment in and downstream of the ionization region, showing an imbalance in positive and negative ion concentrations downstream of a charge conditioner. This study also

measured the positive-to-negative charge ratios of aerosol particles downstream of multiple charge conditioners which showed a charging effect due to ions carried ‘downstream of an ionized region’. The authors used insights from their modelling and ion concentration measurements to support these findings. Lee et al. (2005) measured the concentration and mobility distribution of ions downstream of three charger configurations: a soft X-ray bipolar charger, a charger with one ^{241}Am source (82 μCi), and a charger with two ^{241}Am sources (164 μCi). That study also measured the total charge fraction and positive-to-negative charge ratio of aerosol particles, and determined the X-ray produced a more ‘symmetric’ bipolar charge distribution than the ^{241}Am chargers by producing positive and negative ions with closer electrical mobilities. Johnson et al. (2020) measured individual charge fractions of spherical particles and found good agreement with conventional charging theory (Wiedensohler, 1988) at low flow (0.6 L min $^{-1}$) through a Kr85 bipolar charge conditioner. In that study, deviations from conventional steady-state charge fractions were found for different tubing lengths (8, 33, and 200 cm) and flow rates (1.2 L min $^{-1}$ vs 0.6 L min $^{-1}$), further supported by direct measurements of positive net ion concentrations downstream of the charge conditioner. However, it was concluded that the deviations were either because the particles had not reached a steady-state within the bipolar charge conditioner, as discussed in Alonso et al. (2001), or due to the effect of downstream ions as discussed in Hoppel and Frick (1990).

Hoppel and Frick (1990) discuss the effect of downstream ions in detail, motivated by confusing results in attempts to experimentally validate the charge state achieved by bipolar charge conditioners. The authors included numerical studies of the evolution and attainment of steady-state, with some numerical results for discharging effects. Furthermore, they showed experimental studies of the charge state within and downwind of a “region of high ionization”. In the region downwind of the ionization source, where discharging occurs, Hoppel and Frick (1990) note that “no true equilibrium charge distribution can be maintained”. They demonstrated a mechanism of unequal wall loss of positive and negative ions both numerically and experimentally to support this claim. They also varied the distance of insertion of an outlet tube into a charging region and outlet tube diameter and reported some values for particle charge ratio. To show the discharging effect experimentally, Hoppel and Frick (1990) tested a charger with two different downstream lengths (referred to as “short” and “long NRL ionizer”). From insights gained in the modeling and these different tests, the authors presented a design of a charge conditioner that attained, under design conditions, a unity ratio of negative to positive charges on test particles from 8 nm to 100 nm. Their study focused on achieving this symmetric charge. However, this charge symmetry may reduce performance in aerosol applications, such as lowering the single charge fraction for SMPS measurements or the net charge for low-cost monitoring. Furthermore, it does not represent the significant negative asymmetry of the resulting particle charge distribution from typical bipolar charge conditioners under common operating conditions that are currently widely used, as quantified in this study.

Hoppel and Frick (1990) uses a sufficiently complex numerical model on which

the present work’s model is based, yet, did not quantitatively show the full effects of ion imbalance on discharging particles using the model. Additionally, the authors did not directly compare results of the particle charging model with their experimental data and instead used the model to provide insights into the experimental findings. Despite Hoppel and Frick (1990)’s seminal work on these topics, their findings have largely been overlooked in the design and application of bipolar charge conditioners to date.

In this work, the effect of the discharging regime is quantified and characterized, along with the charging and steady-state regimes, by deriving analytical equations, applying numerical models and performing experimental validation using particle mean charge. We also identify that time in each regime is a main consideration for the bipolar charging process, and experimentally and numerically vary the times in each regime (i.e., by varying volumetric flow rate, tube diameters and tube lengths) to explore the charging regime and discharging regime. Furthermore, our study also varies particle concentration at the same operating conditions to demonstrate independence from particle concentration as assumed in traditional bipolar charging theory.

These results provide a quantitative framework of analytical, numerical and experimental methods and define terminology for viewing bipolar charging, interpreting new experimental results, designing new charge conditioners and validating new models. Further, this work describes approaches to preserve the significant asymmetry in the charge distribution to improve the designs of bipolar charge conditioners for both low-cost monitors and high-resolution instrumentation for particle measurements.

2 Model

2.1 Analytical

2.1.1 Mean charge of a bipolar charge distribution at steady-state

A steady-state bipolar charge distribution is typically centered near neutral. However, it is well known that negative charge fractions are typically higher than positive charge fractions for each integer charge level (e.g., $N_{-3} > N_{+3}$) at steady-state. In air, the mobility of negative ions is typically higher in magnitude than that of positive ions (Leppä et al., 2017). Thus, even if positive and negative gaseous ions are present in equal concentrations, negative ions are more likely to transfer charge to particles by diffusion than positive ions, making the overall distribution of charges asymmetric towards negatively charged particles (Hoppel and Frick, 1990). This imbalance towards negative polarity is quantified by the mean charge, calculated as the first moment of the charge distribution, i.e., $\bar{q} = (\sum qN_q)/N_{\text{tot}}$. In this way, mean charge represents the asymmetry of the particle charge distribution over time. Since mean charge is an average over each individual charge state, a steady-state value of mean charge indicates it is comprised of a steady-state charge distribution (Adachi et al., 1983). Thus, the mean charge is useful and simple for indicating if steady-state is

maintained when the system is subject to varying ion pair concentrations or the time for ion-particle interactions.

A flow of aerosol particles carrying a net electrical charge may be measured as an electrical current. The electrical current (i ; [A]) is equal to the mean charge per particle ($\bar{q}$) multiplied by the number concentration of particles (N ; [m⁻³]), the volumetric flow rate (Q ; [m³ s⁻¹]) and the constant elementary charge (e ; 1.602176634 × 10¹⁹ [C]),

$$i = \bar{q}NQe. \quad (1)$$

Mean charge, $\bar{q}$, can be determined, for example, by measuring N (e.g., using a Condensation Particle Counter) and i (e.g., by using a Faraday Cup Electrometer) at a known flow rate, Q .

The mean charge per particle carried by aerosol particles at a steady-state, bipolar charge distribution is given by the following equation (Nishida et al., 2020; Gunn, 1954), valid for particle diameters $\gtrsim 50$ nm (Wiedensohler, 1988):

$$\bar{q}_{ss} = \frac{2\pi\epsilon_0 kT}{e^2} \ln \left(\frac{n_+ Z_+}{n_- Z_-} \right) \bar{d}. \quad (2)$$

Assuming an equal concentration of ions ($n_+ = n_-$), the mean charge per particle at steady state, $\bar{q}_{ss}$, is a function of mean particle diameter for spherical particles ($\bar{d}$), temperature (T ; [K]) and ratio of electrical mobilities (Z ; [m² V⁻¹ s⁻¹]) of positive (+) to negative (-) ions along with the permittivity of free space (ϵ_0 ; 8.854187817 × 10¹² [F/m]) and Boltzmann constant (k ; 1.380658 × 10⁻²³ [m² kg s⁻² K⁻¹]).

Thus, measuring mean charge, $\bar{q}$, indicates the asymmetry of the bipolar charge distribution caused by a ratio of ion mobilities and ion concentrations, i.e., $\frac{n_+ Z_+}{n_- Z_-}$, assuming that a steady-state charge distribution has been reached and applying Eq 2. By controlling particle diameter, Eq. 2 was validated experimentally by Nishida et al. (2020), i.e., mean charge was demonstrated to be linear with particle diameter and the slope of mean charge as a function of particle diameter was used to determine the ratio of ion mobilities, $\frac{Z_+}{Z_-}$, assuming ions are present in approximately equal concentrations. In that work, the ratio of ion mobilities was applied as a calibration factor to determine lung-deposited surface area (LDSA) from measured current, i . However, for any bipolar charge conditioner, the ion mobility ratio can be used to determine the particle charge distribution as a function of particle diameter (Chen and Jiang, 2018). For example, Wiedensohler (1988) applies an ion mobility ratio of $\frac{Z_+}{Z_-} = 0.875$ and uses Fuchs' charging theory to determine charge fractions used in SMPS inversions. Therefore, a system which measures mean charge for a given particle diameter can be used to estimate the charge distribution at steady-state.

2.1.2 Mean charge in the charging regime

With knowledge of mean charge at steady-state, measurements of mean charge in the charging regime can be used to indicate progress towards reaching steady-state (Adachi et al., 1983).

An aerosol with an initial mean charge ($\bar{q}_{\text{in}}$) develops to a steady-state mean charge ($\bar{q}_{\text{ss}}$) as a function of the nt_{ion} product, which is the product of the concentration of ions (n ; $[\text{m}^{-3}]$) and interaction time between ions and particles (t_{ion} ; $[\text{s}]$). While nt product is a common term, this study carefully specifies that this is the time in the ionization region of the bipolar charge conditioner (t_{ion}) and not the overall time (t) that the particles and ions interaction, including time downstream of the ionization region (t_{d}). The following equation for mean charge in the charging regime was derived for this work from equations shown in Gunn (1954),

$$\frac{\bar{q} - \bar{q}_{\text{ss}}}{\bar{q}_{\text{in}} - \bar{q}_{\text{ss}}} = \exp\left(-\frac{e}{\varepsilon_0} Z n t_{\text{ion}}\right) \quad (3)$$

where it is assumed that during charging the ion electrical mobilities for each polarity are not significantly different (i.e., $Z_+ \approx Z_- \approx Z$) and ion concentrations are equal (i.e., $n_+ \approx n_- \approx n$) as assumed in Gunn (1954) to simplify the charging equation. Positive and negative ions are generated at equal rates from alpha or beta ion sources used in common bipolar charge conditioners. Ion-ion recombination also removes positive and negative ions at equal rates, leaving a constant concentration of free ions of both polarities if ion generation and recombination are dominant, e.g., compared to ion wall losses (Ibarra et al., 2020) or losses by charge transfer to particles (Cooper and Reist, 1973). Therefore, constant ion concentrations of both polarities are commonly assumed for regions of ion production within bipolar charge conditioners (Liu and Pui, 1974; Adachi et al., 1985). Mean charge at steady-state, $\bar{q}_{\text{ss}}$, may be determined using Eq. 2, assuming equal ion concentrations (i.e., $n_+ = n_- = n$) and unequal electrical mobilities (i.e., $Z_+/Z_- \neq 1$) as done in Section 2.1.1. Ion pair production can occur within the charging region, e.g., via a radioactive source, or ions can be transported into a charging region by other means, resulting in the same assumption of equal ion concentrations (Adachi et al., 1980).

It is noted that the effective charging time, τ_{ch} , to reach steady-state is (Gunn, 1954)

$$\tau_{\text{ch}} = \frac{\varepsilon_0}{e Z n} \quad (4)$$

and, importantly, it does not depend on the particle size or the initial charge (Hinds, 1999, Section 15.7). Therefore, Eq. 3 can be expressed as,

$$\frac{\bar{q} - \bar{q}_{\text{ss}}}{\bar{q}_{\text{in}} - \bar{q}_{\text{ss}}} = \exp\left(-\frac{t_{\text{ion}}}{\tau_{\text{ch}}}\right). \quad (5)$$

Equation 5 has been applied in other forms in classical diffusion theory when field charging may be neglected as done in the present work (Fjeld et al., 1990). Assuming a symmetric charge distribution at steady-state (i.e., $\bar{q}_{\text{ss}} = 0$), Eq. 5 is used as an indicator of whether a steady-state is reached in Hinds (1999, Eq. 15.33) and in Vivas et al. (2008, Eq. 13),

$$\bar{q} = \bar{q}_{\text{in}} \exp\left(-\frac{t_{\text{ion}}}{\tau_{\text{ch}}}\right). \quad (6)$$

Furthermore, assuming $\bar{q}_{\text{in}} = 0$, Eq. 5 is used to model charging time from an initially neutral particle to its steady-state (Gunn, 1954; Liu and Pui, 1974),

$$\bar{q} = \bar{q}_{\text{ss}} \left[1 - \exp \left(-\frac{t_{\text{ion}}}{\tau_{\text{ch}}} \right) \right]. \quad (7)$$

Thus, Eq. 5 derived in this work, provides an analytical equation of mean charge of particles in the charging regime that can be obtained without resorting to solving a complete set of numerical equations. Using this equation, mean charge for any asymmetric charge distribution (i.e., $\bar{q}_{\text{ss}} \neq 0$) can be used to indicate progress towards reaching a steady-state (e.g., to characterize whether steady-state is reached as a function of flow rate) which is a common need in characterizing commercial charge conditioners. Additionally, measurements of mean charge can be applied in Eq. 5 to solve for nt_{ion} product of a given charge conditioner and it delineates the charging regime from the steady-state regime.

2.1.3 Mean charge in the discharging regime

Equation 5 assumes a constant ratio of $\frac{n_+ Z_+}{n_- Z_-}$, or more practically speaking, $\frac{n_+}{n_-}$ of Eq. 2. While the ion concentration ratio n_+/n_- is constant in the ion generation region of most charge conditioners (as explained in Section 2.1.2), n_+/n_- changes rapidly downstream of the charging region. This shift in ion concentration ratio depends on the rate of ion-ion recombination, diffusional ion loss to walls, and losses due to electrostatic repulsion. Therefore, if ions are not rapidly removed, n_+/n_- is no longer constant, thereby changing $\bar{q}_{\text{ss}}$ and discharging occurs. This assumption violation of Eq. 5 is reflected by it becoming a singularity in the limit case of unipolar charging. Furthermore, the concentration of particles (which act as an ion sink) becomes significant, whereas it can often be safely neglected in the charging region. To capture all these interrelated effects of the discharging regime, an analytical model is no longer sufficient (e.g., Eq. 5 is no longer valid), and a numerical model is necessary.

2.2 Numerical

A numerical model is introduced which considers the electrical charging and transport phenomena relevant to bipolar charge conditioners. This model is applied to verify the analytical models and aid in interpreting experimental results.

2.2.1 Governing Equations

A numerical model is applied to estimate the concentrations of particles and ions within and downstream of a bipolar charge conditioner. The steady-state conservation equations for the number of monodisperse particles of a given charge level, q , and gaseous ions of a single positive or negative charge in a differential control volume are given as:

$$\nabla \cdot (\vec{u}N_q) = \nabla \cdot (D\nabla N_q) - \nabla \cdot (Z_q\vec{E}N_q) + S_{q,\beta} \quad (8a)$$

$$\nabla \cdot (\vec{u}n_i) = \nabla \cdot (D_i\nabla n_i) - \nabla \cdot (Z_i\vec{E}n_i) + S_{i,\beta} + S_{i,\alpha} + S_{i,q^*} \quad (8b)$$

where N_q is the concentration of particles of a given size and material at q charge level, n_i is the concentration of ions with i charge level, $\vec{u}$ is the bulk velocity of the carrier gas (assumed to be the same for both the carrier gas and particles), D is the particle or ion diffusivity. The contribution to the transport of particles or ions resulting from an electric field is represented by the particle or ion electric mobility, Z , subject to the electric field, $\vec{E}$. The terms denoted as S are the source/sink terms for ion-particle charge transfer, where the subscript β involves charge transfer between particles and ions, and α involves collisions between ions. The final term S_{i,q^*} accounts for ion generated within the system from the ion source. For example, ions may be created by collisions of alpha- or beta-radioactive particles with gas molecules and subsequently transfer charge to a sample of particles.

The source/sink terms, S , represent the rate of increase or decrease in the number concentration of ions and particles at each charge level during bipolar diffusion charging in a method referred to as a birth-and-death model (Boisdrion and Brock, 1970). For example, if a negative ion, n_{-1} , attaches to a particle with a single positive charge, N_{+1} , the particle reduces to a neutral charge level, N_0 , and the gaseous molecule which comprised the ion is torn off (Fuchs, 1963). Here, we assume that the concentrations of neutral gas molecules greatly exceed those of ions or charged particles ($n_0 \gg n_i$), so that the concentrations of neutral gas molecules remain unchanged.

For a monodisperse aerosol of known diameter and particle properties, the source terms in Eq. 8 are given as follows:

$$S_{q,\beta} = \beta^{q+1 \rightarrow q} N_{q+1} n_{-1} - \beta^{q \rightarrow q-1} N_q n_{-1} + \beta^{q-1 \rightarrow q} N_{q-1} n_{+1} - \beta^{q \rightarrow q+1} N_q n_{+1} \quad (9a)$$

$$S_{i,\beta} = - \sum_{q=q_{\min}}^{q_{\max}} \beta^{q \rightarrow q+i} N_q n_i \quad (9b)$$

$$S_{i,\alpha} = -\alpha n_{-1} n_{+1} \quad (9c)$$

$$S_{i,q^*} = q^* \quad (9d)$$

where $\beta^{q \rightarrow q+1}$ is the attachment coefficient for the charge transfer from a positive ion to a particle of charge level, q , for example. The attachment coefficient is a function of particle diffusivity and electrostatic potential, and is calculated using the method given by Reischl et al. (1996), which builds on Fuchs' original work (Fuchs, 1963) and key modifications to the collision probability by Hoppel and Frick (1986), with the specific implementation described in detail in Woo et al. (2022). It is noted collision coefficients from more recent Langevin Dynamics models can be applied over a wide range of conditions (Li and Gopalakrishnan, 2021; Gopalakrishnan et al., 2013). The

ion-ion attachment coefficient is set as a commonly accepted value of $\alpha=1.6\times 10^{12} \text{ m}^3 \text{ s}^{-1}$ (Liu and Pui, 1974), though it should be noted more recent experiments and models show this parameter can vary significantly (Franchin et al., 2015; Tamadate et al., 2020). In the charging region, ions are created with an ion generation rate, q^* , which is equal for both polarities. The full, three-dimensional governing equations may be solved using numerical methods for given boundary conditions as described in Woo et al. (2022). For the current purposes, a simplified model in one-dimensional form is considered using a set of explicit assumptions and solved numerically.

2.2.2 Electrophoresis

A net charge carried by particles and/or ions in a given volume is related to the local electric field through Gauss’s Law. This electric field, in turn, affects the motion of charged particles and ions in a phenomenon typically referred to as electrostatic dispersion (Kasper, 1981; Vemury et al., 1997), electrostatic diffusion (Adachi et al., 1981), or a ‘space charge’ effect (Yu, 1977). For example, an electrostatic force may repel like-charged particles away from one another and, therefore, increase particle losses to walls compared to when particles are uncharged, or affect particle trajectories in instruments such as the DMA (Alonso and Kousaka, 1996) or ELPI (Marjamäki et al., 2005).

In this work, the effect of space charge in bipolar charge conditioners is highlighted. For example, if negative ions are preferentially lost to walls due to their higher diffusion coefficient, an attractive electrophoretic force may prevent further loss of negative ions. Additionally, in that case, a repulsive electrophoretic force may promote loss of positive ions. In this way, space charge will limit the imbalance in ion concentrations caused by diffusion losses (Hoppel and Frick, 1990).

Gauss’s Law in differential form is

$$\nabla \cdot \vec{E} = \frac{\rho}{\varepsilon_0 \varepsilon_r} \quad (10)$$

where ρ is the space charge density, or the concentration of charges per unit volume, ε_0 is the permittivity of free space, and ε_r is the relative permittivity, which is 1 for air. Assuming concentrations of ions are significantly higher than charged particles, the charged particles may be neglected in calculating ρ , resulting in (Hoppel and Frick, 1990),

$$\rho = (n_{+1} - n_{-1}) e. \quad (11)$$

This assumption is valid for the relatively low particle concentrations applied in this work of $<5.14\times 10^5$ particles per cm^3 relative to steady-state ion concentrations of $>8.6\times 10^6$ ions per cm^3 resulting in a ratio of $N_+/n < 0.06$ over all cases. The contribution to space charge from charged particles and the resulting electrophoretic effects on charged particles (rather than ions) is considered in other works (Kasper, 1981; Vemury et al., 1997).

2.2.3 One-Dimensional Numerical Model

In this work, we model the dynamics of ions and particles and the interactions between them as the bulk aerosol flow proceeds through and downstream of the charge conditioner. We consider one-dimensional transport as ions and particles advect in the axial direction through the charger and tubing and consider diffusion losses of ions and space charge effects on ions in the radial direction. For this analysis, an externally applied electric field, e.g., in an ion trap, is not considered. Additionally, we consider losses of particles due to diffusion and space charge effects to be negligible, which is valid for the relatively large (i.e., 239 nm particles) in this work. The distance coordinate in the x direction is transformed into a convective time by applying $dt = dx/\vec{u}$ for axial velocity $\vec{u}$ in plug flow, assuming diffusion and electrophoresis in the axial direction are negligible relative to advection. Thus, by combining Equations 8-11, the particle and ion concentration equations reduce to the following balance:

$$\frac{dN_q}{dt} = \beta^{q+1 \rightarrow q} N_{q+1} n_{-1} - \beta^{q \rightarrow q-1} N_q n_{-1} + \beta^{q-1 \rightarrow q} N_{q-1} n_{+1} - \beta^{q \rightarrow q+1} N_q n_{+1} \quad (12a)$$

$$\frac{dn_{+1}}{dt} = q^* - \alpha n_{-1} n_{+1} - \sum_{q=q_{\min}}^{q_{\max}} \beta^{q \rightarrow q+1} N_q n_{+1} - \frac{4D_{+1}}{r^2} n_{+1} - \frac{Z_{+1}e}{\varepsilon_0} (n_{+1} - n_{-1}) n_{+1} \quad (12b)$$

$$\frac{dn_{-1}}{dt} = q^* - \alpha n_{-1} n_{+1} - \sum_{q=q_{\min}}^{q_{\max}} \beta^{q \rightarrow q-1} N_q n_{-1} - \frac{4D_{-1}}{r^2} n_{-1} - \frac{Z_{-1}e}{\varepsilon_0} (n_{-1} - n_{+1}) n_{-1} \quad (12c)$$

where r is the radius of the cylinder through which the aerosol is flowing. The electrophoresis term of Eqn 8b is converted to one-dimensional form by combining with Eqs. 10 and 11, assuming plug flow in a cylindrical tube and assuming the charge concentration is uniform over a given cross-section, i.e., $\nabla \rho = 0$ in the radial direction (Kasper, 1981; Wilson, 1947; Yu, 1977). The electrophoresis term is applied in the same form in other works for particles (Adachi et al., 1981; Vemury et al., 1997) and ions (Hoppel and Frick, 1990). The diffusion term of Eqn. 8b is converted to one-dimensional form by assuming the ion distribution in a given cylindrical cross-section has one averaged, bulk value and applying the boundary condition that ion concentration is zero at the wall. Then, the net diffusional flux of ions from the bulk volume through a cylindrical surface (i.e., to the cylinder wall) is calculated using a surface area-to-volume ratio for a finite cylindrical cross-section. The derivation of the diffusion term is found in Maisels et al. (2003) and applied in Nishida et al. (2017). Further details of the ion diffusion loss term and its agreement with Gormley and Kennedy (1948) are described in the Supplementary Information.

The diffusion loss term is always negative in the ion balance, i.e., there is a net flux of ions from the bulk aerosol radially to walls. The electrophoresis term is negative if electrostatic repulsion occurs and positive if electrostatic attraction occurs. Thus, space charge effects will moderate any imbalance in concentrations of positive ions

relative to negative ions caused by differences in ion diffusion loss rates (Hoppel and Frick, 1990). A condition is implemented in the numerical model that the sum of the diffusion and electrophoresis terms must be equal to or less than zero, i.e., enforcing a net loss of ions to walls. This condition is a form of boundary condition which is implemented because there cannot be a net attraction of ions from the tubing walls since the walls are considered an ideal sink (not a source) for ions, i.e., electrically conductive and grounded. Therefore, with some exceptions, the present numerical model is largely the same as the birth-and-death model implementation of Hoppel and Frick (1990)’s seminal work. This similarity provides an opportunity for code verification which is discussed further in Sec. 2.3.

2.2.4 Geometry, conditions and solution method

The ordinary differential equations shown in Eqn. 12 are solved simultaneously in Matlab using the ode45 function for integration. Equation 12a is solved simultaneously for all charge levels from $q_{\min}=-7$ to $q_{\max}=+7$ such that all significant concentrations for 239 nm particles are considered. The initial conditions are that ion concentrations are zero and all particles are initially neutral at the inlet, i.e., at $t = 0$, $n_{+1} = 0$, $n_{-1} = 0$ and $N_0 = N$. Once Eqn. 12a is solved, mean charge, $\bar{q}$, is calculated from the integral sum of the individual charge fractions, i.e., $\bar{q} = (\sum qN_q)/N_{\text{tot}}$.

The geometry of the TSI 3077A charging region, the TSI 3077A outlet tubing, and downstream conductive tubing were implemented in the model. Within the TSI 3077A, jetting and recirculation of flows occurs such that the plug flow assumption is not strictly valid within the charge conditioner (de La Verpilliere et al., 2015), therefore the TSI 3077A geometry could not be used directly. Recently, computational fluid dynamics (CFD) methods were applied by the present authors and others, and compared with experimental data to quantify residence time distributions in the TSI 3077A bipolar charge conditioner and its effect on throughput of charged particles (Nishida et al., 2022). It was demonstrated that significant jetting and recirculation occurs due to an adverse pressure gradient created within the geometry. At 1.5 L min^{-1} , a median residence time of $\approx 1\text{-}3$ seconds was found experimentally and compared with ≈ 1 second using CFD methods, agreeing with an average residence time of 1 second found in a previous model (de La Verpilliere et al., 2015). Therefore, in this work, a 1-second charger residence time is assumed for 1.5 L min^{-1} . The flow jet within the TSI 3077A is assumed to have a cylindrical volume with length equal to the internal length of the TSI 3077A, estimated to be 0.15 m (TSI Inc., 2003). Applying a plug flow assumption for a jet assumed to have cylindrical shape gives an effective cylinder diameter of 14.57 mm within the TSI 3077A. The inner diameter of the bipolar charge conditioner (BCC) outlet was 4.6 mm and 50 mm long. A range of tubing lengths and diameters connected to the BCC outlet were used to vary convective time downstream of the BCC at each flow rate. Further geometry details of the experiment and model are found in the Supplementary Information, including a schematic.

For model verification with Wiedensohler (1988), a constant ion concentration

of $n_{+1} = n_{-1} = 1 \times 10^{12} \text{ m}^{-3}$ is imposed. The ion electrical mobilities are set to $Z_+ = 1.35 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, $Z_- = 1.6 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the mass of positive and negative ions are set to 140 and 101 AMU (Atomic Mass Units), respectively (Wiedensohler, 1988). The numerical model is compared with individual charge fractions calculated using the classical approximation of Wiedensohler (1988) where $\frac{Z_+}{Z_-} = 0.875$ for verification.

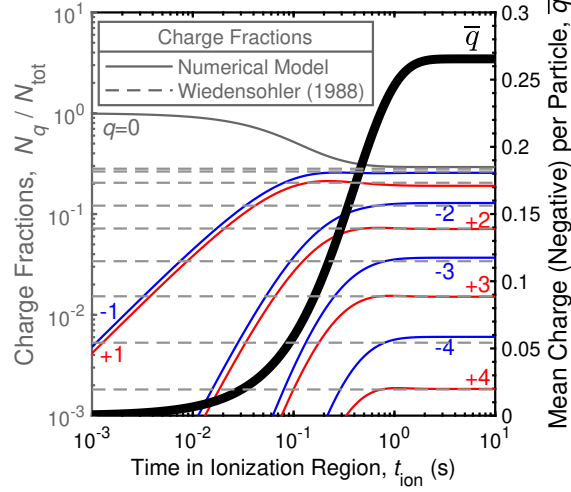
For comparisons with experimental data, a constant ion generation rate in the ionization region of $q^* = 1.3 \times 10^{14} \text{ m}^{-3} \text{ s}^{-1}$ is used for both polarities as previously measured for a TSI 3077A charger (de La Verpilliere et al., 2015). A constant ion mobility is modelled for each ion polarity, though it is known that ions are present in distributions of ion mobilities. Positive and negative ion mobilities of $Z_+ = 0.8 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $Z_- = 1.5 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, were selected based on agreement with experimental data, and the Kilpatrick relation was used to calculate ion masses (Kilpatrick, 1971). These ion mobilities agree well with the peaks of mobility distributions of ions recently produced by a Kr-85 charger using particle-free laboratory air as the sample (Leppä et al., 2017, SI), though a range of ion mobilities have been recorded in previous literature (Tigges et al., 2015). The results section further discusses the effect of ion mobilities and compares the results against the classical approximations (Wiedensohler, 1988).

2.3 Model Verification

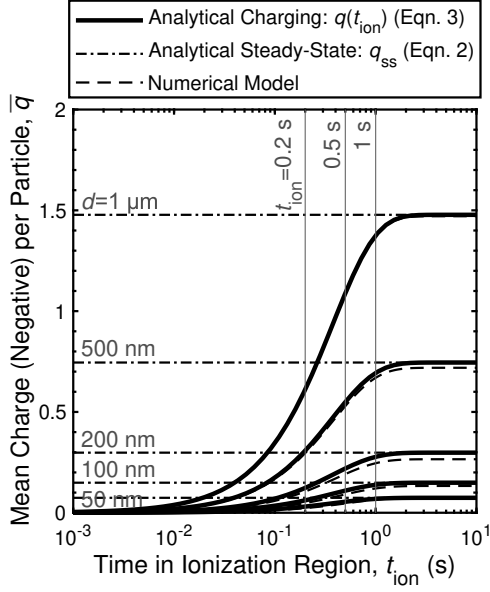
2.3.1 Verification with Classical Steady-State Approximation

Figure 2a shows individual charge fractions dynamically changing as a function of convective time (or residence time) as a steady-state charge distribution develops. Initially uncharged ($q=0$), 200 nm spherical particles acquire charges by ion-to-particle charge transfer. As expected, the fraction of uncharged particles relative to total concentration, N_0/N_{tot} , decreases over time, while the charge fractions of particles at the other integer charge levels, q , increase over time. In this case, steady-state particle charge levels are reached in the order of one second. Figure 2a also shows that the mean charge from the numerical model dynamically changes over convective time in the charging regime, highlighting the negative asymmetry of the overall charge distribution.

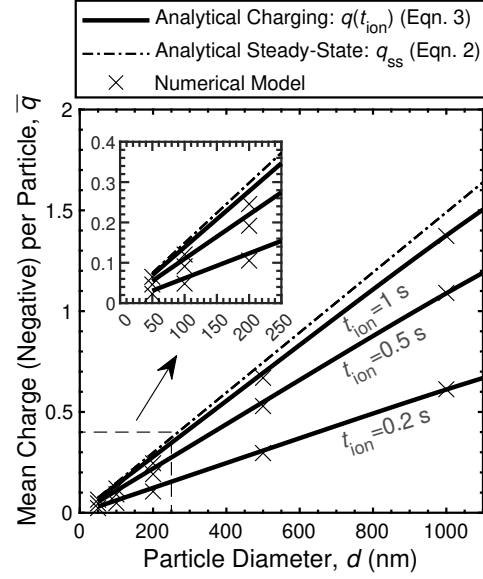
Figure 2a shows convective time from zero to 10 seconds in the ionization region of the charge conditioner (t_{ion}). For the numerical model in this instance, a constant ion concentration of $n_{+1} = n_{-1} = 1 \times 10^{12} \text{ m}^{-3}$ is imposed, and the diffusion and electrostatic terms are not used to align with the assumptions of the classical approximation (Wiedensohler, 1988) used for verification. Therefore, the nt_{ion} product ranges from zero to $10^7 \text{ ions cm}^{-3} \text{ s}$. The numerical model shows good agreement with the classical approximation in the steady-state regime and, therefore, supports that the complex attachment coefficients and particle conservation equations are implemented correctly. The individual charge fractions of the numerical model are slightly more negative than the classical approximation resulting in a mean charge of



(a)



(b)



(c)

Figure 2: (a) Numerical model of a steady-state charge distribution developing over time for 200 nm particles in comparison with a classical steady-state charge distribution (Wiedensohler, 1988). Mean charge indicates asymmetry of charge distribution and regime of bipolar charging. (b) Mean charge per particle as a function of particle-ion interaction time using analytical Eq. 3 and the numerical model. (c) Mean charge per particle as a function of particle diameter using analytical Eq. 3 and the numerical model.

$\bar{q} = -0.265$ (numerical) compared with $\bar{q} = -0.230$ (approximation) at steady-state. Minor differences are expected since the classical approximation itself was generated by least-square regression to a numerical model based on Fuchs theory (Wiedensohler, 1988).

2.3.2 Verification of Charging Regime Equations

The same numerical model as Section 2.3.1 was applied for mean charge as a function of charging time and particle diameter as shown in Figures 2b and 2c, respectively, to verify the analytical equation for the charging regime (Eqn 3). The numerical model applies ion mobilities of $Z_+ = 1.35 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ and $Z_- = 1.6 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$. Therefore, analytical Eqn 3 is applied using $Z = \frac{Z_+ + Z_-}{2} = 1.475 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ and $\frac{Z_+}{Z_-} = \frac{1.35 \times 10^{-4}}{1.6 \times 10^{-4}} = 0.844$.

Agreement between the analytical and numerical models is excellent for a selection of monodisperse diameters ranging from 50 nm to 1 μm as a function of charging times as shown in Figure 2b. Minor differences in results between the analytical and numerical models are attributed to the more complex attachment coefficients of the numerical model, which are not strictly a function of ion mobility, e.g., also depend on ion mass.

Figure 2c shows mean charge as a function of particle diameter for the analytical and numerical models. Mean charge is a linear function of particle diameter at steady-state as shown in Eqn. 2, which was experimentally validated (Nishida et al., 2020). These results confirm mean charge is also a linear function of particle diameter in the charging regime since the effective charging time of Eq. 4 does not depend on particle size (Hinds, 1999).

The excellent agreement supports the use of Eqn. 3 to represent the charging regime in simple, analytical form. The verification also supports that the numerical model is implemented correctly in the charging regime, at least for constant ion concentrations. Detailed verification of the numerical method, including attachment coefficients, has been performed previously by the present authors and others (Woo et al., 2022) for an open-source implementation of this numerical charging model by comparison with Hoppel and Frick (1990), showing identical agreement. That code verification used attachment coefficients specified in Hoppel and Frick (1990), which were calculated using slightly different ion properties than the present implementation. In this work, Wiedensohler (1988) was chosen for verification to comment directly on its implementation in SMPS inversions.

These model results confirm that in the charging regime, measurements of mean charge can be used to indicate progress towards a steady-state charge distribution. Finally, since the numerical model calculates individual charge fractions and the analytical equation calculates only mean charge, agreement between the two supports that measurements of the mean charge, $\bar{q}$, can represent the entire charge distribution, i.e., individual charge fractions, if it is clearly interpreted that a given charge conditioner is operating in the charging, steady-state, or discharging regime, e.g., by varying flow rate and experimentally measuring $\bar{q}$ for a known $\bar{q}_{\text{in}}$.

3 Experiments

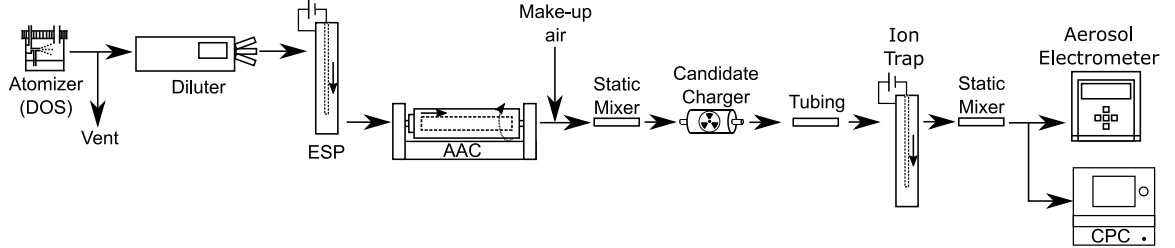


Figure 3: Experimental setup for measuring mean charge per particle from a candidate charger at a controlled number concentration and particle diameter. The method enables varying residence time of ions with particles downstream of the candidate charger by flow varying rate and tubing lengths.

The setup shown in Fig. 3 was used to vary residence time downstream of a charge conditioner’s ionizing region and measure changes in mean charge per particle. Spherical, DOS particles (bis(2-ethylhexyl) sebacate; >97.0%, Aldrich Chemistry) were generated using an atomizer (Model 3076, TSI Inc., Shoreview, MN, USA) with HEPA-filtered, compressed air. After atomization, a liquid trap removed excess liquid and the main aerosol flow from the atomizer was vented. From the main flow, a sample of DOS was passed through a diluter (eDiluter Pro; Dekati Ltd., Kangasala, Finland), which added HEPA-filtered compressed air, to vary the number concentration of measured particles with dilution ratios between 5 and 25. The diluter was bypassed for a no-dilution setting. Then, the sample passed through an electrostatic precipitator (ESP) to remove all charged particles, leaving only uncharged particles in the sample flow. The ESP comprised a long DMA column (3081 DMA; TSI Inc.) operated with zero sheath flow and was set to a voltage sufficient to remove all charged particles using a voltage controller (3080 Electrostatic Classifier; TSI Inc.). The uncharged particles were then classified using an Aerodynamic Aerosol Classifier (AAC; Cambustion Ltd., Cambridge UK), which selects a narrow range of aerodynamic diameters from a polydispersed aerosol (Tavakoli et al., 2014). The AAC enabled control of particle size without relying on or affecting the particle charge. This avoided pre-existing charge on the particles affecting the bipolar charging process. Although, this effect should be negligible on bipolar diffusion charging as previously demonstrated by Equation 4 and the discussion in Section 2.1.2.

A flow of HEPA-filtered, compressed air (make-up air) was controlled with a mass flow controller and added downstream of the AAC to vary flow through the candidate charger while maintaining a constant flow rate through the AAC. A static mixer (1/4-40-3-12-2; Koflo Corporation, USA) was included to ensure the aerosol flow was adequately mixed with the make-up air, to prevent sampling biases downstream (Johnson et al., 2018; Walker et al., 2018). Unless otherwise stated, all tubing used in this experimental setup was 0.25-inch conductive silicone tubing. This tubing was also used upstream of the bipolar charge conditioner being evaluated (candidate

charger), which has been shown to change the ions generated with the conditioner (Asbach et al., 2016). However, this effect was present for both bipolar charge conditioner tested and both agreed with expected charging results (e.g., Wiedensohler (1988)) at 0.3 L/min and 33 cm tube length, which is typical for SMPS operation.

The flow passed through a candidate bipolar charge conditioner to charge the DOS particles. The candidate chargers used were the Model 3077A (TSI Inc.) which produced gaseous ions using a ^{85}Kr source (β decay, 10.76 year half-life) with nominal activity of 10 mCi/370 MBq and the ACC-EL1 (Atmose Ltd.) which used a ^{63}Ni source (β decay, 101 year half-life) with nominal activity of 2.5 mCi/92.5 MBq. Charged particles and ions were convected through the outlet of the candidate charger followed by defined lengths and diameters of conductive silicone (TSI Inc.) or stainless-steel tubing followed by an ion trap (produced by Atmose Ltd.), as summarized by the full experimental matrix shown in the Supplementary Information. Ions convected downstream of the charge conditioner were removed in the ion trap by applying a controlled potential between two electrodes. One electrode of the ion trap is an outer metal cylinder and the other electrode is a concentrically located inner rod.

Downstream of the ion trap, another static mixer (1/4-40-2-6-2; Koflo Corporation, USA) was used to ensure the aerosol was adequately mixed before splitting the flow between two parallel instruments (Johnson et al., 2020; Walker et al., 2018). The two parallel instruments were an aerosol electrometer (Model 3068B; TSI Inc.), used to measure electrical current from a flow of charged particles, i , and a condensation particle counter (CPC; Model 3776; TSI Inc.), used to measure number concentration, N . Flow through the aerosol electrometer was controlled with an external mass flow controller downstream of the aerosol electrometer to improve accuracy in flow rate, Q (as recommended by the manufacturer of the aerosol electrometer). A Gilibrator (Sensidyne, USA) was used to verify the volumetric flow rates in the setup. Thus, the set-up enabled mean charge per particle to be measured as a function of controlled particle diameter and number concentration by applying Eq. 1, i.e., $\bar{q} = \frac{i}{NQ_e}$.

The AAC was set to select particles with a monodisperse aerodynamic diameter, $d_a = 225$ nm, corresponding to particle diameter of $d = 239$ nm. Since the density of DOS of 914 kg m^{-3} is lower than the reference density (1000 kg m^{-3}), particle diameter is larger than aerodynamic diameter. It should be noted that mobility diameter and particle diameter were equivalent since the particles were spheres. It is assumed that any particle losses for these 239 nm particles were equal for all particle charge levels.

The voltage setpoints used for the ESP and ion trap were determined using analytical equations for limited particle trajectory based on the electric field between concentric electrodes and the dimensions of each device. During preliminary system checks, a filter was placed upstream of the charge conditioner and the aerosol electrometer was used to confirm that all gaseous ions were captured by the ion trap at its voltage setpoint for each sample flowrate. Separately, the CPC was used to confirm that particles were not significantly captured in the ion trap. Furthermore, it was confirmed using a CPC and Aerosol Electrometer in parallel that the ESP captured all charged particles at each of its voltage setpoints.

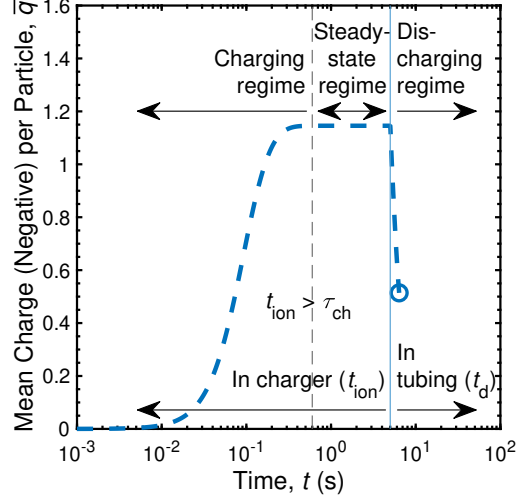
Flow rates were varied between 0.6 L min^{-1} and 10.8 L min^{-1} . A tubing length of 33 cm is standard between the bipolar charge conditioner and DMA column in a common SMPS system (TSI Inc., 2006b). This tubing length was used in comparison to a short piece of tubing of 3 cm between the charger and ion trap and longer lengths of tubing. Varying flow rate changes both the convective time within the charger (t_{ion}) and in tubing downstream (t_d), whereas varying the tubing length or diameter only changes the convective time in tubing downstream of the charger (t_d). This aspect is key for characterizing particle charging in the charging and steady-state regimes relative to the discharge regime. Further details of experimental configurations of varying flow rates and tubing lengths/diameters are shown in the Supplementary Information.

4 Results

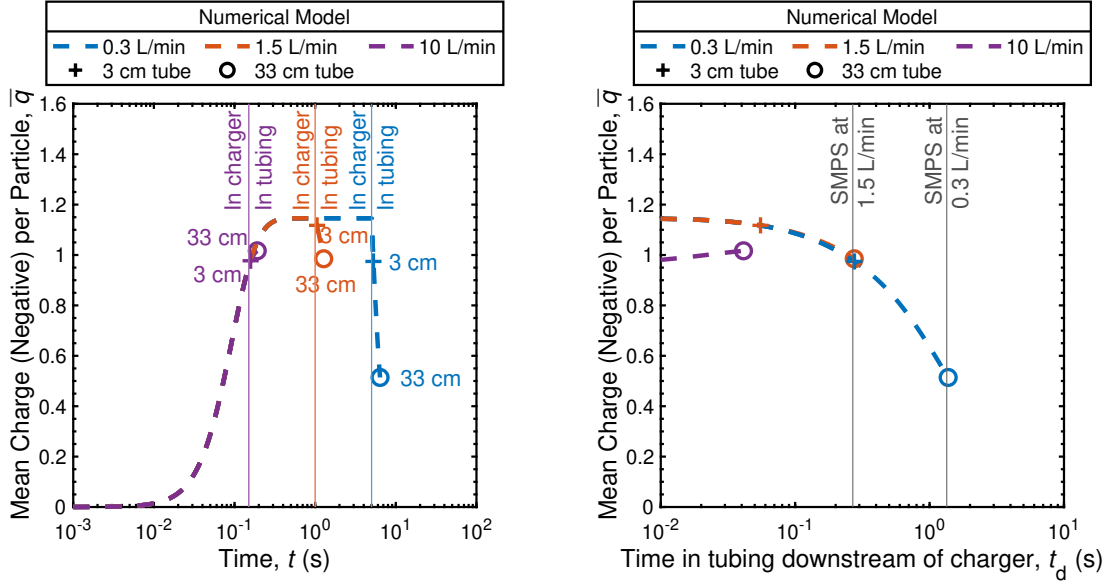
Figure 4a shows numerical results of mean charge, $\bar{q}$, over convective time to delineate the three regimes of bipolar charging. The figure highlights the change in the asymmetry of the charge distribution through the charging, steady-state, and discharging regimes for conditions commonly used in a practical bipolar charge conditioner of 0.3 L min^{-1} flow with a 33 cm length of tubing downstream (TSI Inc., 2006b). For all numerical results, flow rates and tubing lengths are set to match the experimental configuration.

Figure 4b shows numerical model results of mean charge per particle as a function of convective time in the charger (t_{ion}) and downstream of the charger t_d for flow rates of 0.3, 1.5 and 10 L min^{-1} and downstream tubing lengths of 3 cm and 33 cm. Figure 4b shows a steady-state is reached within the charging region for both 0.3 and 1.5 L min^{-1} cases. However, at 10 L min^{-1} , particles exit the charging region still in the charging regime due to insufficient ion-to-particle charging time to reach the steady-state regime (i.e., insufficient nt_{ion} product). Immediately downstream of the charging region, the charge distribution changes rapidly from its state at the exit of the charging region in each case. The final charge state reached depends on the amount of discharging which depends on the downstream volume (i.e., tube diameter and length) and flow rate.

Mean charge as a function of time in the tubing downstream of the charger is shown in Figure 4c. At 0.3 L min^{-1} , the mean charge increases from -1.15 at the outlet of the charging region to -0.97 after 3 cm of tubing and -0.51 after 33 cm of tubing. A more modest change in mean charge is found for 1.5 L min^{-1} . In all cases, ions of both polarities are convected downstream and continue to charge the particles. At 0.3 L min^{-1} , positive and negative ions have concentrations of $n_{+1} = 9.0 \times 10^6 \text{ cm}^{-3}$ and $n_{-1} = 8.9 \times 10^6 \text{ cm}^{-3}$, respectively at the charger exit, however, after 33 cm of tubing, these concentrations reduce to $n_{+1} = 1.4 \times 10^5 \text{ cm}^{-3}$ and $n_{-1} = 4.7 \times 10^4 \text{ cm}^{-3}$, respectively, since negative ions are preferentially lost to tubing walls by diffusion. The higher concentration of positive ions convected with particles in the tubing charges particles more positively. Notably, at 10 L min^{-1} , the



(a)



(b)

(c)

Figure 4: Numerical model results showing mean charge per particle as a function of convective time to (a) highlight three regimes of bipolar charging at 0.3 L min^{-1} and with 33 cm length of downstream tubing. By varying downstream tube length (3 cm vs 33 cm) and flow rate ($0.3, 1.5$ or 10 L min^{-1}), deviations from the steady-state regime are shown as a function of convective time (b) in charger and tubing downstream of charger, and (c) in tubing downstream of charger.

mean charge decreases from -0.97 at the outlet of ionization region to -1.0 after passing through the bipolar charge conditioner outlet and 33 cm of tubing. At 10 L min^{-1} , the characteristic time for ion diffusion losses is lower relative to convective time and both positive and negative ions are carried downstream of the charging region. The preferential loss of negative ions in the downstream tubing is not sufficient to alter the charge distribution more positively, and thus, charging continues in a similar pattern to the charging regime, i.e., charging more negatively. The downstream ions' significantly change the mean charge in less than one second downstream of the ionization region when particles are in the charging regime or steady-state regime upon exiting the charger.

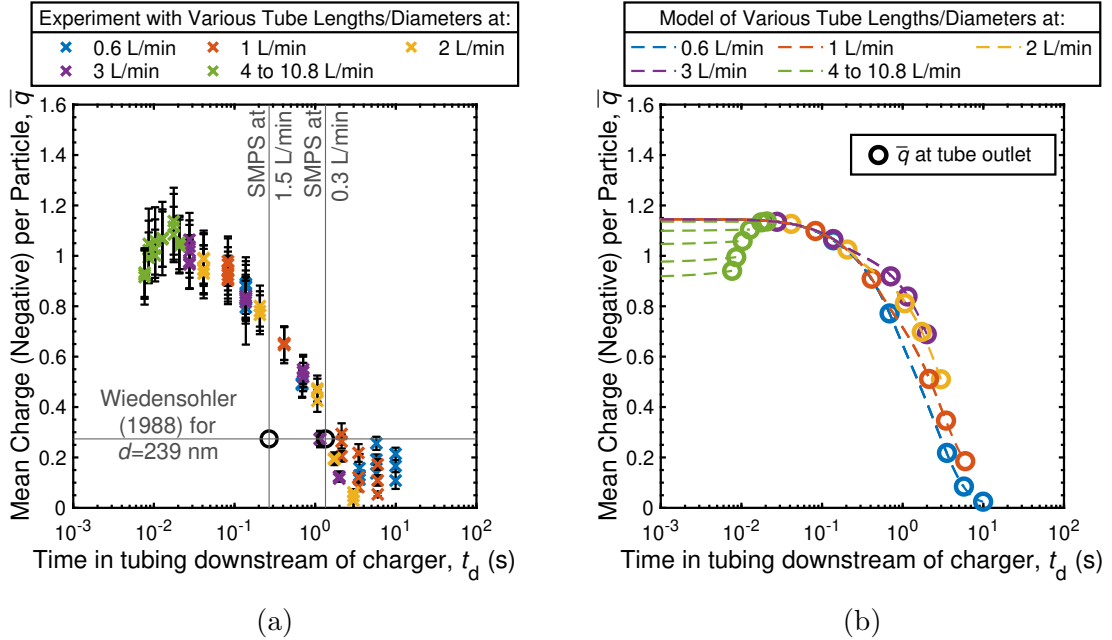


Figure 5: (a) Experimental and (b) numerical results showing mean charge per particle as a function of convective time in tubing downstream of the charger (i.e., convective time between charging region and ion trap). Data were gathered for a wide range of tube lengths and flow rates for the same Kr-85 charger and 239 nm diameter particles.

Figure 5a and 5b show experimental and numerical data, respectively, for the mean charge per particle as a function of convective time in downstream tubing (i.e., residence time in tubing between the charger and the ion trap, including the outlet tube of the charger) for particles of 239 nm in diameter using the TSI 3077A charger. For Figure 5a, a full experimental matrix is shown in the Supplementary Information.

Vertical error bars (estimating the uncertainty, u , with 95% confidence) are shown for all experimental results (Figures 5a and 7) and reflect propagating two standard deviations, σ_i , in the measured current, i , and 10% accuracy in concentration ($u_N/N = 0.1$) measured by the CPC (TSI Inc., 2006a) through Eqn. 1, i.e.,

$u_{\bar{q}} \approx \pm \bar{q} \left((2\sigma_i/i)^2 + (u_N/N)^2 \right)^{1/2}$, for data gathered over 60 seconds of sampling time or longer. Error bars are not shown for numerical results (Figure 2, 4, 5b, 6) given the model’s assumptions introduce unknown uncertainties and that repeatability is not relevant for deterministic models.

For a wide range of convective times, achieved by varying flow rates and downstream tubing lengths/diameters, the consistent curve of Figure 5 demonstrates that convective time downstream of the ionization region of the charge conditioner (t_d) is a key parameter for determining the resulting charge distribution. An initial increase in the magnitude of mean charge per particle, $|\bar{q}|$, is shown for the highest flow rate settings, due to operation in the charging regime. The increase in charge asymmetry as a function of increasing time is characteristic of the charging regime, as described by Eq. 5 and as shown previously by Adachi et al. (1983). Then, a plateau region follows where particles are close to their true steady-state at approximately $\bar{q} = -1$. Both the charging and steady-state regimes could not be maintained experimentally using the TSI 3077A charge conditioner since its design has a short length of stainless steel tubing at its outlet which is not removable, so some convective time between the charger and an external ion trap is unavoidable. After the plateau region, $|\bar{q}|$ decreases with increasing convective time between the charger and ion trap due to the more significant effect of ‘downstream ions’. Input particle number concentration was varied by dilution (from 1.37×10^3 to 5.14×10^5 particles per cm^3) to produce the different data points at each convective time. For downstream convective times longer than ~ 1 second, the scatter between data points increases due to increased sensitivity to particle number concentration.

Assuming the mean charge at steady-state, $\bar{q}_{ss}$, is most accurately reflected at the plateau region of 5a by an average of measurements between 3 and 8 L min^{-1} , results in $\bar{q}_{ss} = -1.01$. For the 10.8 L min^{-1} case, which is clearly in the charging regime, measurements show $\bar{q} = -0.927$. Applying Eq. 5, assuming an average ion mobility of $1.15 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$, results in an estimated nt_{ion} product of $1.18 \times 10^{12} \text{ m}^{-3} \text{s}$ for the 10.8 L min^{-1} case. This result is comparable to an integrated nt_{ion} product predicted by the numerical model of $1.20 \times 10^{12} \text{ m}^{-3} \text{s}$ for the same conditions. Further, Eq. 5 estimates that an nt_{ion} product of $2.2 \times 10^{12} \text{ m}^{-3} \text{s}$ is required to reach 99% of steady-state for the same ion properties.

Measurement systems such as the SMPS assume the aerosol is at a steady-state charge distribution with known values (Wiedensohler, 1988). Specifically, the assumed charge levels used in commonly used SMPS systems correspond to a mean charge of -0.27 for 239 nm particles (see horizontal line labeled Wiedensohler in Fig. 5a) for both low (0.3 L min^{-1}) and high (1.5 L min^{-1}) flow rates using a standard 33 cm length of tubing downstream of the charge conditioner (TSI Inc., 2006b). The mean charge of the charge distribution assumed in SMPS inversions aligns with measured mean charge for convective times in tubing near 1.375 s (‘low flow’). However, applying a linear interpolation between averaged measurements of $\bar{q}$ at 1 L min^{-1} and 2 L min^{-1} and 33 cm tubing, yields $\bar{q} = -0.72$ for 1.5 L min^{-1} . The $\bar{q} = -0.72$ corresponds to a charge distribution which is significantly more asymmetric than assumed in SMPS

inversions at ‘high flow’, where $\bar{q} = -0.27$. Furthermore, the experimentally measured steady-state is approximately $\bar{q} = -1$, which is nearly a factor of 4 higher in magnitude than $\bar{q} = -0.27$ which is assumed to be at steady-state (Wiedensohler, 1988).

The experimental data of Fig. 5a and numerical model of Fig. 5b show good qualitative agreement in delineating the three regimes considering the complexity of the phenomena involved. Differences between the model and experiment are attributed to limitations in the model in the critical region downstream of the charger. In reality, ions have distributions of electrical mobilities and diffusivities. Within the charging region, ions of higher mobility have the most effect on charging due to the increased rate of ion-particle charge transfer. In the downstream region, ions of higher mobility are more readily lost to walls and the remaining ions would shift to lower mobilities on average. In this work, the differences in quantitative agreement are attributed to the assumption of one constant ion diffusivity for each polarity in both the charging region and downstream rather than full distributions of ion properties. Furthermore, the flow in the tubing was assumed to be plug flow while the actual flow in the tubing is laminar and parabolic once it is fully developed. Also, undeveloped flow will occur immediately downstream of the charger and at the connections between different types of tubing which will result in non-uniform flow profiles. Additionally, the distribution of aerosol residence times within the charge conditioner would cause particles to be exposed to a distribution of nt_{ion} products. For that reason, some particles may have reached steady-state within the charging region whereas others may not have, potentially affecting both the ordinate and abscissa of Fig. 5. Despite these potential effects, for the purposes of explaining the experimental data, the agreement is considered sufficient to provide an initial basis for further study of more complex models and experiments.

Figure 6 shows numerical results of individual charge fractions achieved at steady-state within the charging region, immediately downstream of 3 cm of tubing, and downstream of 33 cm of tubing. The shape of the bipolar charge distribution is typical of a Gaussian distribution where particles are increasingly less likely to carry charge levels further from neutral. As described in Section 2.1.1, the charge distribution is asymmetric towards negative charge levels and results show the steady-state is significantly more negative than assumed in SMPS inversions. Downstream of 3 cm of tubing, some discharging occurs shifting the particles more positive in each charge level as well as on average. Discharging becomes significant using the 33 cm tube. The +1 single charge fraction increases from 0.093 at steady-state to 0.159 (71% increase) after 33 cm of tubing due to charging from positive ‘downstream ions’. The significant change in the +1 single-charge fraction has implications for SMPS inversions which rely most on the +1 single-charge fraction for determining number concentration from SMPS scans.

Figure 7 shows mean charge per particle as a function of time downstream of the Atmos ACC-EL1 compared with that of the TSI 3077A. The Atmos ACC-EL1 and has a different internal geometry and ion source than the TSI 3077A charger, yet still generates ions of both polarities which are convected downstream of its outlet tube. While the internal geometry of the ACC-EL1 was not modelled in this work, the same

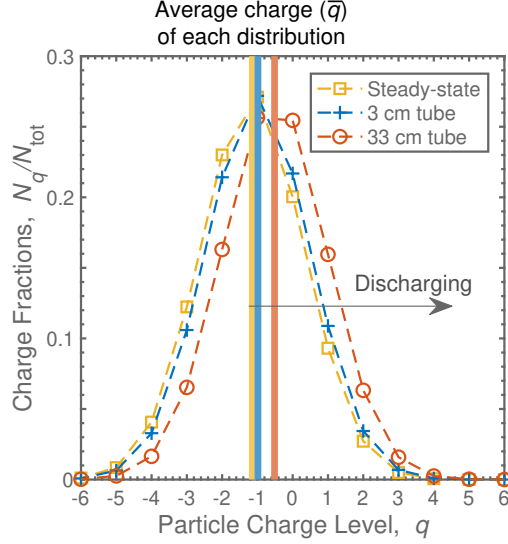


Figure 6: Numerical results for changes in charge fractions of 239 nm diameter particles from steady-state during discharging for different lengths of tubing at a volumetric flow rate of 0.3 L min^{-1} . Changes in positive single-charge fraction (+1) are of particular note because these changes are most significant for resulting SMPS size distribution.

reduction in magnitude of mean charge is observed and is attributed to the discharging regime. The similar results for both candidate chargers provides further evidence that the three bipolar charging regimes are generic to bipolar diffusion charging and not unique to a specific charger geometry or ion source.

5 Discussion

Characterizing the three charge regimes provides a basis for further study of the most dominant effects in practical bipolar charge conditioners. This study can be applied to design improved charge conditioners and interpret aerosol measurements.

The results show the characteristics of the charging regime, as described by Eq. 5, for an nt_{ion} product which is insufficient to reach steady-state ($t_{\text{ion}} < \tau_{\text{ch}}$). These findings are made possible by using mean charge as a metric for determining whether a steady-state is reached, as was done previously by Adachi et al. (1983). The analytical relationship between mean charge and nt_{ion} product, derived in this work for an asymmetric charge distribution, is used to quantitatively predict the nt_{ion} product when operated in the charging regime ($nt_{\text{ion}} = 1.18 \times 10^{12} \text{ m}^{-3}\text{s}$ for 10.8 L min^{-1} flow) and estimate the nt_{ion} product required to reach 99% of steady-state ($nt_{\text{ion}} = 2.2 \times 10^{12} \text{ m}^{-3}\text{s}$). Assuming plug flow, these numbers provide an approximate estimate that >99% of steady-state can be reached with 5.8 L min^{-1} flow or lower for the TSI 3077A charge conditioner. This equation provides confidence that mean charge is a

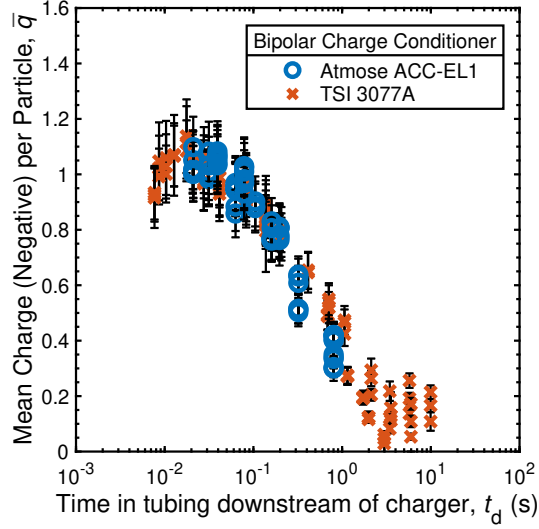


Figure 7: Experimental results showing mean charge per particle from two different bipolar charge conditioners (TSI 3077A and Atmos ACC-EL1) as a function of convective time in tubing downstream of the charger (i.e., convective time between charging region and ion trap). Data were gathered for a wide range of tube lengths and flow rates for 239 nm diameter particles.

clear indicator of whether steady-state is reached and can be applied to quantitatively characterize the operating limits of a given bipolar charge conditioner.

If significant discharging occurs, the final charge levels as a function of particle size are not at a bipolar, steady-state or near steady-state. The discharging regime behaves as a combination of bipolar and unipolar charging causing the final charge fractions to become a distinct function of:

- particle size and concentration (e.g., particles take up ions, making them unavailable for further charging);
- ion concentrations (e.g., ion generation rates);
- volume downstream of the ionization/charging region (e.g., downstream tube volumes);
- tube diameters (due to interaction with electrical space charge and diffusion losses); and
- volumetric flow rate.

Since these parameters cannot all be well-controlled, they introduce uncertainty in the charge fractions and the instruments which rely on the charge fractions. Of particular concern are deviations from an assumed charge distribution due to particle properties, i.e., particle size and number concentration. The experimental results of the present work show that the mean charge per particle varies with number concentration at convective times in downstream tubing longer than ~ 1 s (e.g., vertical

scatter in datapoints at each convective time in Fig. 5a). This sensitivity is attributed to particles taking up ions making them unavailable for further charging, a process which depends on ion concentrations and particle concentration.

Deviations from the assumed steady-state charge fractions are often attributed to a saturation of the ion source most commonly observed with high particle number concentrations (de La Verpilliere et al., 2015; Ibarra et al., 2020). Parameters such as the ion-to-particle number concentration ratio are used to determine when this effect is significant. By quantifying effects of the discharging regime, the present work demonstrates that clear interpretation of the three regimes of common bipolar charge conditioners must be considered if attempting to quantify deviations from steady-state, e.g., using high particle concentrations or low nt_{ion} charge conditioners.

The discharging methods considered in this work have parallels in spatial afterglows in plasma systems. After exiting a plasma, particle charge rapidly changes in the afterglow because high mobility electrons, which control charge within the plasma, are depleted much faster than ions (Vidwans et al., 2023; Suresh et al., 2021). In photoelectric charge conditioners, negative ions produced from photoionization recombine with the resulting positively charged particles downstream of a photoionizing region (Maisels et al., 2002, 2003). In both distinct cases, electric fields can be applied to control the eventual charge state (Vidwans et al., 2023; Nishida et al., 2017). Due to the importance of the discharging region and similarity in other fields, further analysis of the dynamics of that process is warranted.

Models of ion-to-particle charging in bipolar charge conditioners should be validated using experimental data which is carefully controlled and interpreted considering the three regimes of bipolar charging. Data from the TSI 3077A charger aligns with the widely-used charge distributions from Wiedensohler (1988) when the convective time in downstream tubing is approximately 1 second or longer. It is noted that particles pass through a relatively large volume at the inlet of a DMA column prior to reaching the electrodes, resulting in significant time for discharging to occur at both low and high flow rates. As such, though the Wiedensohler approximation may be appropriate in many cases (Wiedensohler, 1988), care must be taken in applying it for measurement inversions if the charge conditioner is subject to the sensitivities of the discharging regime listed above.

Furthermore, if discharging is present in experimental data but not accounted for in models (e.g., by incorrectly assuming steady-state), the models may be incorrectly validated. The present work clearly shows that steady-state is not the effective mode of operation of a common bipolar charge conditioner. The framework of the three regimes provides a basis for correct validation of more detailed models of ion-particle interactions as well as 3-dimensional charging and transport models.

Finally, the three regimes should be considered in the design of new charge conditioners for a range of applications. The sensitivities of the discharging regime may be completely avoided by quickly removing ions downstream of the ionization/charging region. Then, operating with a more asymmetric steady-state than traditionally expected could provide advantages. For example, SMPS systems could be run with negative polarity, thereby increasing absolute signals (since the negative charge frac-

tions are significantly higher in magnitude than the positive charge fractions). In the design of a low-cost electrometer-based monitor, the asymmetry in charge can be harnessed, in this case increasing signal strength by nearly a factor of nearly four from that previously assumed (Nishida et al., 2020).

6 Conclusion

Charge distributions must be known as a function of particle size for widely used aerosol measurement systems. In this work, we quantify a significant phenomenon that affects bipolar charge distributions and characterize three regimes of bipolar charging for a common Kr-85 bipolar charge conditioner (TSI 3077A). We show that although a ‘steady-state regime’ is reached within the charge conditioner, the charge distribution is significantly more negative than expected: mean charge carried by 239 nm particles was approximately $\bar{q} = -1$ compared to $\bar{q} = -0.27$ expected by conventional theory. Using analytical, numerical and experimental techniques, we demonstrate that gaseous ions are readily convected into tubing downstream of the charge conditioner, causing significant deviation from steady-state in a ‘discharging’ regime. We quantify this surprisingly significant effect and show mean charge changes by nearly a factor of four within one second. We demonstrate that the discharging effect is primarily a function of the time the particles and remaining free ions interact downstream of the charger’s ionization region by varying the length/diameter of the downstream tubing and sample flow rate. This effect is also demonstrated by a different bipolar charge conditioner with a different internal geometry and ion source than the 3077A charger. We discuss how all three regimes of charging, steady-state and discharging should be considered in the design and operation of bipolar charge conditioners with the aim of improving accuracy in aerosol systems such as differential mobility analyzing systems and low-cost aerosol monitors.

Acknowledgements

We thank Kerry Chen for his assistance in the lab. Robert Nishida and Jason Olfert acknowledge funding support from Transport Canada. Tyler Johnson acknowledges and appreciates the significant support of the Postdoctoral Fellowship from Natural Sciences and Engineering Research Council of Canada (NSERC).

Potential competing interests

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Robert Nishida and Tyler Johnson each have a financial interest in Atmos Ltd.

Bibliography

- Adachi, M., Kousaka, Y., and Okuyama, K. (1985). Unipolar and bipolar diffusion charging of ultrafine aerosol particles. *Journal of Aerosol Science*, 16(2):109–123.
- Adachi, M., Okuyama, K., and Kousaka, Y. (1981). Electrostatic coagulation of bipolarly charged aerosol particles. *Journal of Chemical Engineering of Japan*, 14(6):467–473.
- Adachi, M., Okuyama, K., and Kousaka, Y. (1983). Electrical neutralization of charged aerosol particles by bipolar ions. *Journal of Chemical Engineering of Japan*, 16(3):229–235.
- Adachi, M., Okuyama, K., Kousaka, Y., and Takahashi, T. (1980). Electrical charging of uncharged aerosol particles under at bipolar ion concentrations. *Journal of Chemical Engineering of Japan*, 13(1):55–60.
- Adachi, M., Pui, D. Y., and Liu, B. Y. (1993a). Aerosol charge neutralization by a corona ionizer. *Aerosol science and technology*, 18(1):48–58.
- Adachi, M., Pui, D. Y. H., and Liu, B. Y. H. (1993b). Aerosol charge neutralization by a corona ionizer. *Aerosol Science and Technology*, 18(1):48–58.
- Alonso, M., Alguacil, F., Nomura, T., and Kousaka, Y. (2001). Examination of after-charging effects downstream of an aerosol neutralizer. *Journal of aerosol science*, 32(2):287–294.
- Alonso, M. and Kousaka, Y. (1996). Mobility shift in the differential mobility analyzer due to brownian diffusion and space-charge effects. *Journal of aerosol science*, 27(8):1201–1225.
- Asbach, C., Kaminski, H., Lamboy, Y., Schneiderwind, U., Fierz, M., and Todea, A. M. (2016). Silicone sampling tubes can cause drastic artifacts in measurements with aerosol instrumentation based on unipolar diffusion charging. *Aerosol Science and Technology*, 50(12):1375–1384.
- Biskos, G., Reavell, K., and Collings, N. (2005). Description and theoretical analysis of a differential mobility spectrometer. *Aerosol Science and Technology*, 39(6):527–541.
- Boisdrón, Y. and Brock, J. (1970). On the stochastic nature of the acquisition of electrical charge and radioactivity by aerosol particles. *Atmospheric Environment (1967)*, 4(1):35–50.
- Chen, X. and Jiang, J. (2018). Retrieving the ion mobility ratio and aerosol charge fractions for a neutralizer in real-world applications. *Aerosol Science and Technology*, 52(10):1145–1155.

- Cooper, D. W. and Reist, P. C. (1973). Neutralizing charged aerosols with radioactive sources. *Journal of Colloid and Interface Science*, 45(1):17–26.
- de La Verpilliere, J. L., Swanson, J. J., and Boies, A. M. (2015). Unsteady bipolar diffusion charging in aerosol neutralisers: A non-dimensional approach to predict charge distribution equilibrium behaviour. *Journal of aerosol Science*, 86:55–68.
- Fierz, M., Houle, C., Steigmeier, P., and Burtscher, H. (2011). Design, calibration, and field performance of a miniature diffusion size classifier. *Aerosol Science and Technology*, 45(1):1–10.
- Fissan, H., Helsper, C., and Thielen, H. (1983). Determination of particle size distributions by means of an electrostatic classifier. *Journal of Aerosol Science*, 14(3):354–357.
- Fjeld, R., Wu, D., and McFarland, A. (1990). Evaluation of continuum regime theories for bipolar charging of particles in the 0.3-13 μm diameter size range. *IEEE transactions on industry applications*, 26(3):523–528.
- Flagan, R. C. (1998). History of electrical aerosol measurements. *Aerosol science and technology*, 28(4):301–380.
- Franchin, A., Ehrhart, S., Leppä, J., Nieminen, T., Gagné, S., Schobesberger, S., Wimmer, D., Duplissy, J., Riccobono, F., Dunne, E., et al. (2015). Experimental investigation of ion-ion recombination under atmospheric conditions. *Atmospheric Chemistry and Physics*, 15(13):7203–7216.
- Fuchs, N. A. (1963). On the stationary charge distribution on aerosol particles in a bipolar ionic atmosphere. *Geofisica Pura E Applicata*, 56(1):185–193.
- Gopalakrishnan, R., Meredith, M. J., Larriba-Andaluz, C., and Hogan Jr, 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. and Kennedy, M. (1948). Diffusion from a stream flowing through a cylindrical tube. In *Proceedings of the Royal Irish Academy. Section A: Mathematical and Physical Sciences*, volume 52, pages 163–169. JSTOR.
- Gunn, R. (1954). Diffusion charging of atmospheric droplets by ions, and the resulting combination coefficients. *Journal of Atmospheric Sciences*, 11(5):339–347.
- Han, B., Hudda, N., Ning, Z., Kim, H.-J., Kim, Y.-J., and Sioutas, C. (2009). A novel bipolar charger for submicron aerosol particles using carbon fiber ionizers. *Journal of Aerosol Science*, 40(4):285–294.

- He, M. and Dhaniyala, S. (2014). Experimental characterization of flowrate-dependent bipolar diffusion charging efficiencies of sub-50 nm particles. *Journal of aerosol science*, 76:175–187.
- Hinds, W. C. (1999). *Aerosol technology: properties, behavior, and measurement of airborne particles, 2nd Ed.* John Wiley & Sons.
- Hoppel, W. and Frick, G. (1990). The nonequilibrium character of the aerosol charge distributions produced by neutralizers. *Aerosol Science and Technology*, 12(3):471–496.
- Hoppel, W. A. and Frick, G. M. (1986). Ion—aerosol attachment coefficients and the steady-state charge distribution on aerosols in a bipolar ion environment. *Aerosol Science and Technology*, 5(1):1–21.
- Ibarra, I., Rodríguez-Maroto, J., and Alonso, M. (2020). Bipolar charging and neutralization of particles below 10 nm, the conditions to reach the stationary charge distribution, and the effect of a non-stationary charge distribution on particle sizing. *Journal of Aerosol Science*, 140:105479.
- Intra, P. and Tippayawong, N. (2011). An overview of unipolar charger developments for nanoparticle charging. *Aerosol and Air Quality Research*, 11:187–209.
- ISO (2009). BS ISO 15900: 2009 (E) Determination of particle size distribution—differential electrical mobility analysis for aerosol particles.
- Johnson, T., Nishida, R., Irwin, M., Symonds, J., S. Olfert, J., and Boies, A. (2018). Agreement Between Different Aerosol Classifiers Using Spherical Particles. In *Cambridge Particle Meeting*, Cambridge, UK. June 15, 2018.
- Johnson, T. J., Nishida, R. T., Irwin, M., Symonds, J. P., Olfert, J. S., and Boies, A. M. (2020). Measuring the bipolar charge distribution of nanoparticles: Review of methodologies and development using the aerodynamic aerosol classifier. *Journal of Aerosol Science*, 143:105526.
- Johnson, T. J., Nishida, R. T., Zhang, X., Symonds, J. P., Olfert, J. S., and Boies, A. M. (2021). Generating an aerosol of homogeneous, non-spherical particles and measuring their bipolar charge distribution. *Journal of Aerosol Science*, 153:105705.
- Kaminski, H., Kuhlbusch, T. A. J., Fissan, H., Ravi, L., Horn, H.-G., Han, H.-S., Caldow, R., and Asbach, C. (2012). Mathematical description of experimentally determined charge distributions of a unipolar diffusion charger. *Aerosol Science and Technology*, 46(6):708–716.
- Kasper, G. (1981). Electrostatic dispersion of homopolar charged aerosols. *Journal of Colloid and Interface Science*, 81(1):32–40.

- Kilpatrick, W. (1971). An experimental mass-mobility relation for ions in air at atmospheric pressure. In *Proc. Annu. Conf. Massspectrosc*, volume 19, pages 320–325.
- Knutson, E. and Whitby, K. (1975). Accurate measurement of aerosol electric mobility moments. *Journal of aerosol science*, 6(6):453–460.
- Kousaka, Y., Adachi, M., Okuyama, K., Kitada, N., and Motouchi, T. (1983). Bipolar charging of ultrafine aerosol particles. *Aerosol Science and Technology*, 2(4):421–427.
- Kwon, S., Sakurai, H., Seto, T., and Kim, Y. (2006). Charge neutralization of sub-micron aerosols using surface-discharge microplasma. *Journal of Aerosol Science*, 37(4):483–499.
- Lee, H. M., Kim, C. S., Shimada, M., and Okuyama, K. (2005). Bipolar diffusion charging for aerosol nanoparticle measurement using a soft x-ray charger. *Journal of Aerosol Science*, 36(7):813–829.
- Leppä, J., Mui, W., Grantz, A. M., and Flagan, R. C. (2017). Charge distribution uncertainty in differential mobility analysis of aerosols. *Aerosol Science and Technology*, 51(10):1168–1189.
- Li, L. and Gopalakrishnan, R. (2021). An experimentally validated model of diffusion charging of arbitrary shaped aerosol particles. *Journal of Aerosol Science*, 151:105678.
- Li, Y., Chen, X., and Jiang, J. (2022). Measuring size distributions of atmospheric aerosols using natural air ions. *Aerosol Science and Technology*, 56(7):655–664.
- Liu, B. Y. and Pui, D. Y. (1974). Electrical neutralization of aerosols. *Journal of Aerosol Science*, 5(5):465–472.
- Liu, B. Y., Whitby, K. T., and Pui, D. Y. (1974). A portable electrical analyzer for size distribution measurement of submicron aerosols. *Journal of the Air Pollution Control Association*, 24(11):1067–1072.
- Maisels, A., Jordan, F., and Fissan, H. (2002). Dynamics of the aerosol particle photocharging process. *Journal of applied Physics*, 91(5):3377–3383.
- Maisels, A., Jordan, F., and Fissan, H. (2003). On the effect of charge recombination on the aerosol charge distribution in photocharging systems. *Journal of Aerosol Science*, 34(1):117–132.
- Marjamäki, M., Lemmetty, M., and Keskinen, J. (2005). Elpi response and data reduction i: Response functions. *Aerosol Science and Technology*, 39(7):575–582.

- Masson-Delmotte, V., Zhai, P., Pirani, S., Connors, C., Péan, S., Berger, N., Caud, Y., Chen, L., Goldfarb, M., and Scheel Monteiro, P. M. (2021). Ipcc, 2021: Summary for policymakers. in: Climate change 2021: The physical science basis. contribution of working group i to the sixth assessment report of the intergovernmental panel on climate change.
- Murray, C. J., Aravkin, A. Y., Zheng, P., Abbafati, C., Abbas, K. M., Abbasi-Kangevari, M., Abd-Allah, F., Abdelalim, A., Abdollahi, M., Abdollahpour, I., et al. (2020). Global burden of 87 risk factors in 204 countries and territories, 1990–2019: a systematic analysis for the global burden of disease study 2019. *The Lancet*, 396(10258):1223–1249.
- Nishida, R., Boies, A., and Hochgreb, S. (2017). Modelling of direct ultraviolet photoionization and charge recombination of aerosol nanoparticles in continuous flow. *Journal of Applied Physics*, 121(2):023104.
- Nishida, R. T., Johnson, T. J., Hassim, J. S., Graves, B. M., Boies, A. M., and Hochgreb, S. (2020). A simple method for measuring fine-to-ultrafine aerosols using bipolar charge equilibrium. *ACS sensors*, 5(2):447–453.
- Nishida, R. T., Woo, M., Johnson, T. J., and Olfert, J. S. (2022). Quantifying residence times in neutralizers to improve temporal resolution of measurements. *American Association for Aerosol Research 40th Annual Conference*, October 3-7, 2022, Raleigh, USA.
- Reischl, G. P., Mäkelä, J. M., Karch, R., and Necid, J. (1996). Bipolar charging of ultrafine particles in the size range below 10 nm. *Journal of Aerosol Science*, 27(6):931–949.
- Stommel, Y. and Riebel, U. (2004). A new corona discharge-based aerosol charger for submicron particles with low initial charge. *Journal of Aerosol Science*, 35(9):1051–1069.
- Suresh, V., Li, L., Felipe, J. R. G., and Gopalakrishnan, R. (2021). Modeling nanoparticle charge distribution in the afterglow of non-thermal plasmas and comparison with measurements. *Journal of Physics D: Applied Physics*, 54(27):275205.
- Tamadate, T., Higashi, H., Seto, T., and Hogan, C. J. (2020). Calculation of the ion–ion recombination rate coefficient via a hybrid continuum-molecular dynamics approach. *The Journal of Chemical Physics*, 152(9).
- Tavakoli, F., Symonds, J. P. R., and Olfert, J. S. (2014). Generation of a monodisperse size-classified aerosol independent of particle charge. *Aerosol Science and Technology*, 48(3):i–iv.
- Ten Brink, H., Plomp, A., Spoelstra, H., and Van de Vate, J. (1983). A high-resolution electrical mobility aerosol spectrometer (mas). *Journal of aerosol science*, 14(5):589–597.

- Tigges, L., Jain, A., and Schmid, H.-J. (2015). On the bipolar charge distribution used for mobility particle sizing: Theoretical considerations. *Journal of Aerosol Science*, 88:119–134.
- TSI Inc. (2003). Models 3077/3077a aerosol neutralizers, instruction manual, p/n 1933077, revision m. *TSI*.
- TSI Inc. (2006a). Model 3776 ultrafine condensation particle counter: Operation and service manual, revision b.
- TSI Inc. (2006b). *Series 3080 Electrostatic Classifiers: Operation and Service Manual, Revision G*.
- Vemury, S., Janzen, C., and Pratsinis, S. E. (1997). Coagulation of symmetric and asymmetric bipolar aerosols. *Journal of Aerosol Science*, 28(4):599–611.
- Vidwans, A., Dhawan, S., and Biswas, P. (2023). An atmospheric pressure plasma afterglow to charge ultrafine aerosol particles. *Physica Scripta*, 98(11):115401.
- Vivas, M. M., Hontanon, E., and Schmidt-Ott, A. (2008). Design and evaluation of a low-level (0.24 μCi) radioactive aerosol charger based on ^{241}Am . *Journal of aerosol science*, 39(3):191–210.
- Walker, D., Johnson, T. J., Nishida, R. T., Symonds, J. P. R., and Reavell, K. (2018). Uniformity of Particle Concentration after Mixing Aerosol Flows. In *10th International Aerosol Conference*, St. Louis, USA. September 7, 2018.
- Wang, S. C. and Flagan, R. C. (1990). Scanning electrical mobility spectrometer. *Aerosol Science and Technology*, 13(2):230–240.
- White, H. J. (1951). Particle charging in electrostatic precipitation. *Transactions of the American Institute of Electrical Engineers*, 70(2):1186–1191.
- Wiedensohler, A. (1988). An approximation of the bipolar charge distribution for particles in the submicron size range. *Journal of Aerosol Science*, 19(3):387–389.
- Wilson, I. B. (1947). The deposition of charged particles in tubes, with reference to the retention of therapeutic aerosols in the human lung. *Journal of colloid science*, 2(2):271–276.
- Woo, M., Schriebl, M. A., Knoll, M., Boies, A. M., Stettler, M. E., Hochgreb, S., and Nishida, R. T. (2022). Open-source modelling of aerosol dynamics and computational fluid dynamics: Bipolar and unipolar diffusion charging and photoelectric charging. *Computer Physics Communications*, 278:108399.
- Yu, C. (1977). Precipitation of unipolarly charged particles in cylindrical and spherical vessels. *Journal of Aerosol Science*, 8(4):237–241.